

DESCRIPTION

STACKED BODY FOR TUBES, AND TUBE CONTAINER

TECHNICAL FIELD

5 **[0001]**

The present invention relates to laminate and the like for forming a tubular container.

BACKGROUND ART

10 **[0002]**

Substrates and ink layers are known to have conventionally been incorporated in tube bodies in order to improve the visibility and appearance of tubular containers. Polyethylene terephthalate (PET) film has typically been used for the substrate in consideration of dimensional stability and printing ease. In addition, the ink layer formed on the PET film and a layer closer to the surface than the ink layer are bonded by an adhesive.

15 **[0003]**

Moreover, the surface of the tube body may be required to have functions such as antistatic properties, matte properties, light resistance, light absorbance or blocking resistance.

20 **[0004]**

More specifically, Patent Document 1 proposes a laminate for tubes having a layered structure consisting of a low-density polyethylene (LDPE) film containing an antistatic agent/polyethylene (PE) adhesive layer/LDPE film/PE adhesive layer/aluminum oxide-deposited PET film//ink layer-PET film/milky white LDPE film/linear low-density polyethylene (LLDPE) layer in that order moving from the front to the back of the laminate. Incidentally, the symbol "/" indicates extrusion lamination while the symbol "//" indicates dry lamination.

30 **[0005]**

Patent Document 1 describes that a PET film provided with an aluminum oxide-deposited PET film and ink layer

is adhered by dry lamination using a two-component-type, polyester-based adhesive (paragraphs [0025] and [0031] of Patent Document 1). In addition, the outermost layer of the tube laminate is formed with an LDPE film in which an
5 antistatic agent has been kneaded therein (paragraphs [0015] and [0017] of Patent Document 1). Thus, as shown in FIG. 1 of the present application, the tube laminate (1) described in Patent Document 1 comprises a layered structure consisting of a PET film//ink layer/PET film in
10 that order moving from the front to the back, and the front side is imparted with antistatic properties.

[0006]

In addition, Patent Document 2 describes an extrusion laminate (9) having a layered structure as
15 shown in FIG. 2(a) of the application, and a dry laminate (10) having a layered structure as shown in FIG. 2(b) of the application. In addition, a PE melted resin layer is used as an extrusion-laminated adhesive layer, while a urethane-based adhesive is used as an adhesive for dry
20 lamination.

[0007]

In Patent Document 2, since a PET film serves as the surface layer, and since the printed side of the PET film and a sealant film are laminated by means of a lamination
25 adhesive, the resulting extruded laminate has a layered structure consisting of a surface layer/adhesive layer/ink layer/sealant layer, in that order, while the resulting dry laminate has a layered structure consisting of a surface layer//ink layer/sealant layer, in that
30 order.

[0008]

Moreover, Patent Document 2 describes that a strength level for practical use can be attained if laminate strength between the surface layer and the ink
35 layer is 1.0 N/15 mm or more.

PRIOR ART DOCUMENTS

Patent Documents

[0009]

Patent Document 1: Japanese Unexamined Patent
Publication No. 2001-38861

Patent Document 2: Japanese Unexamined Patent
5 Publication No. 2012-136582

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0010]

However, if stress is applied to the laminate for
10 tubes described in Patent Document 1 when molding a
shoulder portion of a tube, there was the problem of the
ink layer undergoing cohesive peeling causing the surface
PET film to be peeled off. In addition, since the
laminate for tubes described in Patent Document 1 always
15 requires dry lamination between the aluminum oxide-
deposited PET film and PET film provided with the ink
layer, there is still room for improvement with respect
to handling ease and economic feasibility.

[0011]

20 The tube laminate described in Patent Document 1 is
expected to incur greater costs since an additional film
having an antistatic agent kneaded therein is required to
impart antistatic properties to the front side thereof.

[0012]

25 In addition, Patent Document 2 does not describe
applications of the tubular container. Even if a tubular
container was assumed to be formed using the packaging
material described in Patent Document 2, if the laminate
strength between the surface layer and ink layer is 1.0
30 N/15 mm, the surface layer is predicted to be peeled off
since the tubular container would be unable to withstand
stress generated when molding a shoulder portion of a
tube.

[0013]

35 Functionality of the front side of the extrusion
laminate or dry laminate is not concretely suggested in
Patent Document 2.

[0014]

Thus, an object of the present invention is to provide a laminate for tubes which can solve at least one problem described above, and a tubular container using that laminate for tubes.

Means for Solving the Problems

[0015]

As a result of conducting extensive studies in consideration of the aforementioned problems, the inventors of the present invention completed the inventions as set forth below.

[1] A laminate for tubes having a functional coating layer, a surface layer, an adhesive layer, an ink layer and a laminated substrate laminated in that order moving from the front to back.

[2] The laminate for tubes according to [1], wherein the functional coating layer is formed by coating a varnish containing a functional material onto the surface layer.

[3] The laminate for tubes according to [2], wherein at least a portion of a seal portion of the surface layer is not coated with the varnish containing a functional material.

[4] The laminate for tubes according to [2] or [3], wherein the functional material is an antistatic agent and/or matting agent.

[5] The laminate for tubes according to any one of [1] to [4], wherein the surface layer contains a low-density polyethylene and/or linear low-density polyethylene.

[6] The laminate for tubes according to any one of [1] to [5], wherein the surface layer contains a polyethylene terephthalate film.

[7] The laminate for tubes according to any one of [1] to [6], wherein the adhesive layer is formed with a two-component-type adhesive consisting of a polyol having an ester moiety and a polyisocyanate, the ink layer is

formed with UV ink, and the side of the laminated substrate that contacts the ink layer is formed with a polyolefin.

5 [8] The laminate for tubes according to [7], wherein the polyol having an ester moiety is a polyester polyol.

[9] The laminate for tubes according to [7], wherein the UV ink contains a polyisocyanate.

[10] The laminate for tubes according to [7], wherein the UV ink is UV flexographic ink.

10 [11] The laminate for tubes according to any one of [1] to [10], wherein the laminated substrate comprises a polyethylene terephthalate film.

[12] The laminate for tubes according to any one of [1] to [11], wherein the initial laminate strength
15 between the surface layer and the ink layer is 3.0 N/15 mm or more.

[13] The laminate for tubes according to any one of [1] to [12], wherein the ink layer is located on the surface of the laminated substrate at a location
20 corresponding to a seal portion

[14] The laminate for tubes according to any one of [1] to [13], wherein the ink layer is located over the entire surface of the laminated substrate.

[15] The laminate for tubes according to any one of
25 [1] to [14], wherein the surface layer contains a polyolefin, the adhesive layer is formed with a two-component-type adhesive consisting of a polyol having an ester moiety and a polyisocyanate, the side of the laminated substrate that contacts the ink layer is formed
30 with a polyolefin, and the UV ink layer is located on the surface of the laminated substrate at a location corresponding to a seal portion.

[16] A tubular container having a body portion formed with the laminate for tubes according to any one
35 of [1] to [15].

Effects of the Invention

[0016]

According to the present invention, loss of function or a decrease in laminate strength due to a migration of functional materials from the functional layer to the adhesive layer can be prevented and functionality can be imparted to the front side of a laminate for tubes by laminating a functional coating layer, surface layer and adhesive layer in that order moving from the front to back.

10

Brief Description of the Drawings

[0017]

FIG. 1 is a schematic cross-sectional view of a laminate for tubes described in Patent Document 1.

15

FIG. 2(a) is a schematic cross-sectional view of an extrusion laminate described in Patent Document 2, and FIG. 2(b) is a schematic cross-sectional view of a dry laminate described in Patent Document 2.

FIG. 3 is a schematic cross-sectional view of a laminate for tubes according to an embodiment of the present invention.

20

Embodiments for Carrying out the Invention

[0018]

<Constituent Elements of Laminate for Tubes>

25

The laminate for tubes is a laminate in which a functional coating layer, surface layer, adhesive layer, ink layer and laminated substrate are laminated in that order moving from the front to back.

[0019]

30

The laminate for tubes has a front side facing towards the outside when a tube has been formed, and a back side facing towards the inside when a tube has been formed or facing towards the contents of the tube. The exposed portion of the functional coating layer is able to form the front side. The exposed portion of the laminated substrate is able to form the back side.

35

[0020]

FIG. 3 is a schematic cross-sectional view of one example of the laminate for tubes according to an embodiment of the present invention. As shown in FIG. 3, a functional coating layer (15), a surface layer (16), an adhesive layer (4), an ink layer (5) and a laminated substrate (17) are laminated in that order moving from a front side (2) to a back side (3) of a laminate for tubes (14). The surface layer (16) may have a seal portion (16a) capable of being sealed with the back side (3) of the laminate for tubes (14) when a body portion is formed with the laminate for tubes (14). The laminated substrate (17) may contain a polyolefin surface (17a) and a portion (17b) other than the polyolefin surface.

[0021]

The following respectively provides explanations of the constituent elements of the laminate for tubes in the form of the "functional coating layer", "surface layer", "adhesive layer", "ink layer" and "laminated substrate".

[0022]

<Functional Coating Layer>

The functional coating layer is a layer for imparting functionality to the front side of the laminate for tubes and is formed by coating a functional material.

[0023]

As shown in FIG. 3, the functional coating layer (15) forms the front side (2) of the laminate for tubes (14).

[0024]

Examples of functions imparted to the front side of the laminate for tubes include antistatic properties, matte properties, light resistance, light absorbance, abrasion resistance, lubricity and blocking resistance. Among these, antistatic properties and/or matte properties are preferable. For example, when antistatic properties are imparted, dust attracted to a tubular container due to static electricity is inhibited during packing, transport or displaying, thereby making it

possible to ensure an attractive appearance for a tubular container. In addition, when matte properties are imparted, the tubular container is able to have a high-grade appearance such as a matte finish. Moreover, when
5 both antistatic and matte properties are imparted, both an attractive appearance and matte finish can be realized for a tubular container.

[0025]

The functional coating layer is preferably formed by
10 coating a varnish containing a functional material. The functional material is more preferably dispersed in the varnish. A varnish known in the field of packaging materials or tubular containers may be used.

[0026]

15 For example, the varnish may be over printing (OP) varnish. Although the varnish may be oil-based or UV-curable, it is preferably UV-curable.

[0027]

The varnish containing a functional material can be
20 coated by any arbitrary printing method such as relief printing, planographic printing or intaglio printing.

[0028]

Examples of functional materials include antistatic agents, matting agents, lubricants and anti-blocking
25 agents. Among these, antistatic agents and/or matting agents are preferable.

[0029]

Examples of antistatic agents include anionic surfactants such as carboxylates or sulfonates; cationic
30 surfactants such as amine salts or quaternary ammonium salts; nonionic surfactants such as polyethylene glycol or polyvalent alcohol; electrically conductive powders such as carbon black or metal powders; polymeric antistatic agents such as polyether-polyolefin block
35 copolymers, polythiophene; and betaines.

[0030]

Examples of matting agents include resin beads

formed from urea resin, acrylic resin or urethane resin; silica fine powder; and zeolite.

[0031]

<Surface Layer>

5 The surface layer is a layer that faces the front side when a tube is formed from the laminate for tubes. The surface layer is arranged between the functional coating layer and the adhesive layer.

[0032]

10 As shown in FIG. 3, the surface layer (16) is closer to the back side (3) of the laminate for tubes (14) than the functional coating layer (15).

[0033]

15 The surface layer is a layer that serves as the outermost layer when a tube is formed from the laminate for tubes. The surface layer may be a single layer or a laminate composed by laminating a plurality of layers, and may have a plurality of the same type of layers. The surface layer has at least one film, and optionally has a
20 printing layer, foil stamping layer, anchor coat layer, adhesive layer, barrier layer, sealant layer or any arbitrary combination thereof. The printing layer, foil stamping layer, anchor coat layer, adhesive layer, barrier layer and sealant layer can be respectively
25 located on at least a portion of the layer or film on which they are laminated.

[0034]

30 The surface layer preferably contains a polyethylene terephthalate (PET) film in order to improve the stiffness of the laminate for tubes.

[0035]

35 From the viewpoint of low-temperature sealability (degree of sealing), the surface layer preferably contains a polyolefin and is more preferably a polyethylene film. Examples of polyethylene films include a low-density polyethylene (LDPE) film, linear low-density polyethylene (LLDPE) film, medium-density

polyethylene (MDPE) film, high-density polyethylene (HDPE) film, and the like.

[0036]

As shown in FIG. 3, when forming a body portion with the laminate for tubes (14), at least a portion of the seal portion (16a) of the surface layer (16) is preferably not coated with varnish containing a functional material in order to facilitate sealing between at least a portion of the front side (2) and at least a portion of the back side (3) of the laminate for tubes (14), and as a result thereof, at least a portion of the seal portion (16a) is preferably exposed.

[0037]

The following provides an explanation of the effect of the functional coating layer on the adhesive layer that adheres the surface layer to the ink layer.

[0038]

[Effect of Functional Coating Layer on Adhesive Layer]

Adhesive strength of the adhesive layer is preferably secured by suppressing the influence of the functional coating layer on the adhesive layer that adheres the surface layer and ink layer in order to improve laminate strength between the surface layer and ink layer.

[0039]

Examples of means for suppressing the influence of the functional coating layer on the adhesive layer include "designing the surface layer" and "selecting a functional material" so as to suppress excessive migration of the functional material from the functional coating layer to the adhesive layer.

[0040]

Designing the surface layer preferably includes adjusting the thickness of the surface layer or layering the surface layer.

[0041]

More specifically, a barrier layer is preferably incorporated in the surface layer in order to suppress excessive migration of the functional material from the functional coating layer to the adhesive layer. As a
5 result of incorporating a barrier layer, a layer that inhibits migration is provided between the functional coating layer and adhesive layer.

[0042]

Selecting a barrier layer for the barrier layer that
10 is of the same type of resin as the surface layer resin and has a higher density is simple and therefore preferable in the sense of assuring seal strength. For example, a film obtained by co-extrusion lamination of a material such as HDPE having comparatively high density
15 can be incorporated in the surface layer.

[0043]

In addition, instead of incorporating a barrier layer, excessive migration of the functional material from the functional coating layer to the adhesive layer
20 can be inhibited by dispersing a resin having higher density than the surface layer resin in the surface layer resin, or forming the surface layer resin per se with a high-density resin.

[0044]

25 The coated amount of varnish containing a functional material is preferably about 0.1 g/m² or more or about 0.3 g/m² or more, and the coated amount is preferably about 3 g/m² or less or about 5 g/m² or less.

[0045]

30 Selecting a functional material for the functional coating layer includes, for examples, the use of a functional material that has a low tendency to undergo migration.

[0046]

35 Although examples of functional materials having a low tendency to undergo migration include polymer materials, since hardly any of these materials can be

used as varnishes, a substance having a comparatively large molecular weight that is classified as a low molecular weight surfactant is selected preferably.

[0047]

5 <Adhesive Layer>

The adhesive layer is a layer for adhering the surface layer and ink layer. Although the adhesive layer can be formed from adhesives known in the art of packaging material or tubular container, it is preferably formed by coating a two-component-type adhesive.

[0048]

The coated amount of the two-component-type adhesive is preferably about 3 g/m² or more in order to secure adhesive strength and prevent separation of the laminate during tubing as well as to obtain prescribed content resistance. On the other hand, the coated amount of the two-component-type adhesive is preferably about 5 g/m² or less in consideration of economic feasibility and the upper limit of adhesive strength, and to prevent the generation of a foul odor attributable to defective drying and residual solvent.

[0049]

The two-component-type adhesive is preferably a combination of a polyol having an ester moiety and a polyisocyanate. In such a mode, since laminate strength is improved as a result of the adhesive layer strongly adhering the surface layer and the ink layer, flaking of the laminated surface layer caused by considerable stress generated in the seal portion of a tube can be prevented. As a result, a printed pattern can be formed even on the seam of the tube, and a continuous printed pattern can be formed over the entire surface of the laminated substrate in particular, thereby ensuring an attractive design for a tubular container. The following provides explanations of the "polyol having an ester moiety" and the

[0050]

(Polyol having Ester Moiety)

The polyol having an ester moiety has heat resistance and strong initial tack as well as superior content resistance. Incidentally, initial tack is a property that results in the demonstration of adhesive strength due to the formation of bonds immediately after having contacted an adhered material, and is also referred to as initial adhesion.

[0051]

Since the polyol having an ester moiety has superior content resistance in comparison with a polyol having an ether moiety, it is able to prevent a tubular container from rupturing from a side seam after contents have been filled into the tubular container.

[0052]

Without being bound by the mechanism, since adhesive strength of the two-component-type adhesive prior to the formation of crosslinks by the polyisocyanate depends on the cohesive energy of the main component, a polyol having an ester moiety, which exhibits greater cohesive force than a polyol having an ether moiety, is thought to be advantageous in terms of initial adhesion.

[0053]

The polyol having an ester moiety is preferably a polyester polyol from the viewpoint of crosslinking by the polyisocyanate.

[0054]

(Polyisocyanate)

The polyisocyanate is a compound having at least two isocyanate groups, and forms an oligomer or polymer by crosslinking with the polyol.

[0055]

An aliphatic polyisocyanate having superior light resistance is preferably used for the polyisocyanate in the case of fabricating a laminate for tubes that demonstrates a luxurious sensation, for example.

[0056]

Examples of aliphatic polyisocyanates include aliphatic diisocyanates such as trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, pentamethylene diisocyanate, 1,2-propylene diisocyanate, 1,2-butylene diisocyanate, 2,3-butylene diisocyanate, 1,3-butylene diisocyanate, 2,4,4- or 2,2,4-trimethylhexamethylene diisocyanate, dimer acid diisocyanate or 2,6-diisocyanatohexanoic acid methyl ester; and, aliphatic triisocyanates such as 2,6-diisocyanatohexanoic acid 2-isocyanatoethyl ester, 1,6-diisocyanato-3-isocyanatomethylhexane, 1,4,8-triisocyanatooctane, 1,6,11-triisocyanatoundecane, 1,8-diisocyanato-4-isocyanatomethyloctane, 1,3,6-triisocyanatohexane or 2,5,7-trimethyl-1,8-diisocyanato-5-isocyanatomethyloctane. In addition, the aliphatic polyisocyanate is preferably hexamethylene diisocyanate.

[0057]

In addition, an aromatic polyisocyanate is also used preferably in order to ensure content resistance.

[0058]

Examples of aromatic polyisocyanates include aromatic diisocyanates such as m-phenylene diisocyanate, p-phenylene diisocyanate, 4,4'-diphenyl diisocyanate, 1,5-naphthalene diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-toluidine diisocyanate or 4,4'-diphenyl ether diisocyanate; aromatic triisocyanates such as triphenylmethane-4,4',4''-triisocyanate, 1,3,5-triisocyanatobenzene, 2,4,6-triisocyanatotoluene; and, aromatic tetraisocyanates such as 4,4'-diphenylmethane-2,2',5,5'-tetraisocyanate.

[0059]

<Ink Layer>

The UV ink layer is layer made of ink and is located on the surface layer side of the laminated substrate. An example of the UV ink layer is a printing layer, and the like. The ink layer may be located on the surface of the laminated substrate at a location corresponding to a seal

portion or may be located over the entire surface of the laminated substrate. Here, the location corresponding to a seal portion refers to a region of the laminate serving as a seal portion when the laminate has been sealed in a tubular shape and formed into a tube. In a specific mode of the present invention, a printed pattern can be formed even on the seam of a tube by arranging the ink layer at a location corresponding to a seal portion on the surface of the laminated substrate, and a continuous printed pattern can be formed over the entire surface of the laminated substrate in particular, thereby making it possible to ensure an attractive design for a tubular container.

[0060]

Although the ink may be oil-based ink or UV ink, it is preferably UV ink.

[0061]

The UV ink is an ultraviolet-curable ink, and since it generally does not contain organic volatile compounds such as organic solvents, it is environmentally-friendly, can be cured instantaneously, and is resistant to fading. Thus, UV ink contributes to improvement of productivity and shortening of production time, while also enabling greater energy savings in comparison with heat-dried ink. The UV ink layer may be formed by covering the printed surface of the laminated substrate with a single UV ink, or a UV ink layer may be formed having a pattern or gradation and the like by printing a single UV ink or plurality of UV inks on the printed surface of the laminated substrate.

[0062]

In general, the UV ink contains a photopolymerizable polymer, and as desired, a monomer, photopolymerization initiator and colorant. Examples of colorants include pigments and dyes, and the like.

[0063]

The UV ink preferably has light resistance and heat

resistance, and is more preferably UV flexographic ink in order to ensure printing reproducibility with respect to substrate having various surface characteristics such as a polyolefin substrate.

5 **[0064]**

In addition, a polyisocyanate is preferably added to the UV ink in order to improve adhesiveness of the UV ink to the laminated substrate as well as cohesiveness of the ink. The addition of a polyisocyanate to the UV ink is
10 preferable since it enables the formation of a crosslinked structure between the ink layer and laminated substrate or between the ink layer and the adhesive layer. Furthermore, the polyisocyanate contained in the UV ink may be the same as that contained in the two-
15 component-type adhesive as previously described.

[0065]

Moreover, the initial laminate strength between the ink layer and surface layer is preferably about 3.0 N/15 mm or more and more preferably about 6.0 N/15 mm or more
20 in order to prevent flaking when external force is applied to the laminate for tubes. Incidentally, in the present specification, initial laminate strength refers to laminate strength measured 30 minutes after completion of lamination.

25 **[0066]**

Ink can be printed onto the laminated substrate by, for example, relief printing, planographic printing, intaglio printing, inkjet printing or any other printing method. Among these, relief printing is preferable and
30 flexographic printing is more preferable.

[0067]

<Laminated substrate>

The laminated substrate is a layer that is printed with UV ink. The laminated substrate may be a laminate
35 in which a plurality of layers are laminated, and may contain a plurality of the same type of layers.

[0068]

The laminated substrate may contain, for example, at least one type of material selected from the group consisting of an adhesive, resin, barrier material and sealant.

5 **[0069]**

 The side of the laminated substrate that contacts the ink layer is preferably formed with a polyolefin in order to improve adhesion between the laminated substrate and the ink. In such a mode, since laminate strength
10 between the surface layer and UV ink layer is improved, flaking of the laminated surface layer caused by considerable stress generated in a seal portion of the tube can be prevented. As a result, a printed pattern can be formed even on the seam of a tube, and a
15 continuous printed pattern can be formed over the entire surface of the laminated substrate in particular, thereby making it possible to ensure an attractive design for a tubular container.

[0070]

20 The laminated substrate may be formed of a single or plurality of polyolefin films. In addition, the laminated substrate preferably has a polyolefin film so that the polyolefin film becomes the innermost layer when a tube is formed from the laminate for tubes. Furthermore, the
25 polyolefin film may be the same as that in the surface layer as previously described.

[0071]

 The laminated substrate preferably has a PET film in the portion other than the innermost layer and the face
30 contacted by the ink layer, in order to secure strength of the laminate for tubes.

[0072]

 Examples of the barrier layer in the laminated substrate include a metal foil layer and metal-deposited
35 or inorganic material-deposited layer, and the like.

[0073]

 The sealant layer in the laminated substrate may be

made of a polyolefin such as LDPE or LLDPE.

[0074]

<Production Method of Laminate for Tubes>

5 The laminate for tubes can be produced according to a method that comprises the following steps:

a printing step for forming a UV ink layer by printing UV ink onto a laminated substrate;

10 a lamination step for obtaining a laminate for tubes by adhering the ink layer side of a laminated substrate to a surface layer member,

a coating step for forming a functional coating layer by coating a varnish containing a functional material onto the side of the laminate for tubes having the surface layer member, and

15 an optional aging step for aging the laminate for tubes as needed.

[0075]

20 A laminated substrate having a polyolefin surface is preferably prepared in order to carry out the printing step. Ink is printed at a location corresponding to a seal portion on the polyolefin surface, or ink is printed over the entire polyolefin surface in particular. The printing step can be carried out by any printing methods, preferably by flexographic printing using UV flexographic ink.

[0076]

The lamination step can be carried out by dry lamination of the polyol having an ester moiety and the polyisocyanate using a two-component-type adhesive.

30 **[0077]**

The coating step can be carried out by relief printing such as flexographic printing using a varnish containing a functional material. The order of the lamination step and coating step may be interchanged.

35 **[0078]**

The aging step is continued until there are no longer any substantial fluctuations in laminate strength

between the surface layer and the ink layer, and can be carried out, for example, for 6 days at 40°C.

[0079]

<Tubular Container>

5 The tubular container is a container having a body portion formed of the laminate for tubes.

[0080]

10 The tubular container can be filled with contents such as pharmaceuticals, cosmetics or foods. Examples of contents include toothpaste, moisturizing cream, sunblock, shampoo, hair conditioner, and the like.

[0081]

The tubular container can be produced according to a method comprising the following steps:

15 a step for obtaining a body portion by overlapping the edges of the laminate to seal them, while rolling up the laminate for tubes so that the non-ink printed face of the laminated substrate is on the inside; and,

20 a step for obtaining a tubular container by bonding a shoulder portion and a head portion having a cap portion to the periphery of the opening of the body portion.

[0082]

25 In addition to being able to prevent cohesive peeling of the ink layer and flaking of the surface layer attributable to stress by improving laminate strength between the surface layer and ink layer, the laminate for tubes of the present invention is also able to ensure visual appearances of a tubular container by enabling a printed pattern to be formed even on the seam portion of a tube, and enabling a successive printed pattern to be formed over the entire surface of the laminated substrate in particular. Thus, it is able to achieve the providing of a tubular container in which the body portion thereof is fully printed by surface printing.

35

Examples

[0083]

Experiment 1: Examination of Functional Coating Layer

<Fabrication of Laminates for Tubes>

5 The varnishes, UV ink, adhesive layer, surface layer and laminated substrate indicated in the following Table 1 were prepared for Examples 1 to 3. The UV ink, adhesive, surface layer and laminated substrate indicated in the following Table 1 were prepared for Comparative Example 1.

[0084]

[Table 1]

	Examples			Comp. Ex.
	1	2	3	1
varnish	UV antistatic varnish	UV matt varnish	UV antistatic matt varnish	-
Surface layer	L-103			
Adhesive	two-component-type adhesive			
Main Component	TM-277			
Curing agent	cat-RT86			
UV ink	FDFL + 5 mass% Add.			
Laminated substrate	Layered Structure having wide of 200mm and length of 800mm of LLDPE(50)/LDPE(80)/EAA(20)/AL(12)/EMAA(30)/PET(12)//LLDPE(100) in that order moving from the front to back			

[0085]

15 Explanation of Abbreviations in Table 1

FDFL: Trade name of UV-curable flexographic ink (manufactured by Toyo Ink Co., Ltd.)

Add.: Hexamethylene diisocyanate

20 TM-277: Trade name of ester-based main component (manufactured by Toyo-Morton, Ltd.)

Cat-RT86: Trade name of aliphatic curing agent (manufactured by Toyo-Morton, Ltd.)

L-103: Trade name of LLDPE film (manufactured by Aicello Chemical Co., Ltd., thickness: 90 μm)

UV anti-static varnish: Varnish mixture obtained by adding an antistatic agent in the form of a quaternary alkyl ammonium salt in an added amount of 5 mass% to No. 11 UV LTP FL OP Varnish(Trade name, manufactured by T & K Toka Corp.)

Flexomat varnish: Flexomat OP Varnish AD-BN(Trade name, manufactured by T & K Toka Corp.)

UV antistatic matte varnish: Mixed varnish obtained by adding an antistatic agent in the form of an alkyl ammonium salt in an added amount of 5 mass% to Flexomat OP Varnish AD-BN(trade name, manufactured by T & K Toka Corp.)

EAA: Ethylene-acrylic acid copolymer

EMAA: Ethylene-methacrylic acid copolymer

AL: Aluminum foil layer

Values indicated in parentheses in layered structure: thickness in μm units

[0086]

UV ink was flexographically printed on the surface of the laminated substrate to form an ink layer.

[0087]

Laminates A for tubes were obtained by dry-laminating "L103" film and the ink layer with an adhesive interposed there between in accordance with the production conditions indicated below using a dry lamination apparatus.

(Production Conditions)

Line speed: 30 m/min

Adhesive coated amount: 3.5 g/m²

[0088]

In Examples 1 to 3, the varnishes indicated in Table 1 were coated onto the side containing "L-103" of Laminate A in the coated amounts indicated in Table 2 using a printer. In Comparative Example 1, varnish was not coated onto the side containing "L-103" of Laminate A. Laminates for tubes were obtained in this manner.

[0089]

The laminates for tubes of Example 1 had a layered structure of antistatic varnish layer-LLDPE(90)//ink layer-LLDPE(50)/LDPE(80)/EAA(20)/AL(12)/EMAA(30)/PET(12)//LLDPE(100) in that order moving from the front to back.

5 **[0090]**

The laminates for tubes of Example 2 had a layered structure of UV matt varnish layer-LLDPE(90)//ink layer-LLDPE(50)/LDPE(80)/EAA(20)/AL(12)/EMAA(30)/PET(12)//LLDPE(100) in that order moving from the front to back.

10 **[0091]**

The laminates for tubes of Example 3 had a layered structure of UV antistatic matt varnish layer-LLDPE(90)//ink layer-LLDPE(50)/LDPE(80)/EAA(20)/AL(12)/EMAA(30)/PET(12)//LLDPE(100) in that order moving from the front to back.

15 **[0092]**

The laminates for tubes of Comparative Example 1 had a layered structure of LLDPE(90)//ink layer-LLDPE(50)/LDPE(80)/EAA(20)/AL(12)/EMAA(30)/PET(12)//LLDPE(100) in that order moving from the front to back.

20 **[0093]**

Furthermore, in the aforementioned layered structures, varnish layer-LLDPE (90) indicates that varnish is coated on the front side of the "L-103" film, while ink layer-LLDPE (50) indicates that UV ink is printed on the front side of the laminated substrate.

25 **[0094]**

In addition, a commercially available laminate for tubes having a gravure printing layer was prepared for use as Comparative Example 2. This laminate for tubes had a layered structure consisting of LLDPE(80)/LDPE(25)/PET(12)-ink layer/LDPE(25)/white LDPE/PETSiOx(12)/EMAA(25)/LLDPE(80) in that order moving from the front to back. Furthermore, PETSiOx represents PET vapor-deposited with silicon oxide, while PET(12)-ink layer indicates that ink is printed onto the back side of a PET substrate.

30

35

[0095]

<Evaluation of Laminates for Tubes>

1. Measurement of Initial Laminate Strength between Surface Layer (Polyolefin) and Ink Layer

5 Laminates for tubes were cut to a size measuring 15 mm wide and 150 mm long 30 minutes after fabricating the laminates for tubes of Examples 1 to 3 and Comparative Example 1 to obtain test pieces.

[0096]

10 Each of the test pieces was evaluated for initial laminate strength between the surface layer and ink layer in accordance with the following measurement conditions using Stograph (for E-L) manufactured by Toyo Seiki Kogyo Co., Ltd.

15 (Measurement Conditions)
Clamping width: 50 mm
Pulling speed: 150 mm/min
Type of peeling: T-peeling

[0097]

20 2. Measurement of Laminate Strength after Aging
The laminates for tubes of Examples 1 to 3 and Comparative Examples 1 and 2 were aging over the course of 6 days at 40°C.

[0098]

25 The aged laminates for tubes were cut to a size measuring 15 mm wide and 150 mm long to obtain test pieces.

[0099]

30 Laminate strength after aging was measured between the surface layer and ink layer for the test pieces of Examples 1 to 3 and Comparative Example 1 in accordance with the same measurement conditions as those used for initial laminate strength using Stograph (for E-L) manufactured by Toyo Seiki Kogyo Co., Ltd., while
35 laminate strength after aging was measured between the printed surface of the "PET-ink layer" and the LDPE layer there beneath for the test piece of Comparative Example

2.

[0100]

3. Evaluation of Destaticizing Properties

Tube bodies were prepared from the laminates for
5 tubes. The charge half-life of the tube bodies was
measured as shown below in accordance with a half-life
measuring method (JIS L 1094).

[0101]

The tube bodies were allowed to stand undisturbed
10 over the course of 24 hours in an environment at a
temperature of 23°C and relative humidity of 50%.
Subsequently, the amount of time until the electrostatic
potential of the tube bodies decreased to 1/2 the initial
value was measured while applying a voltage of 10 kV
15 thereto using a Static Honest Meter ("S-5109", trade
name: Shishido Electrostatic, Ltd.).

[0102]

Destaticizing properties of the tube bodies were
evaluated in accordance with the criteria indicated
20 below.

(Criteria)

G: Time for electrostatic potential of tube body to
decrease to 1/2 of less than 10 seconds

NG: Time for electrostatic potential of tube body to
25 decrease to 1/2 of 10 seconds or more

[0103]

4. Soiling Test

Tube bodies were fabricated from the laminates for
tubes. The tube bodies were allowed to stand undisturbed
30 over the course of 24 hours in an environment at a
temperature of 23°C and relative humidity of 50%.
Subsequently, the tube bodies were placed in a toner-type
dirt chamber (Ueki Kosakusho Co., Ltd.) followed by
rotating a fan to cause dirt to adhere to the tube bodies
35 over the course of 5 minutes. Subsequently, the tube
bodies were removed and the degree of soiling of the tube
bodies was observed and evaluated in accordance with the

criteria indicated below.

(Criteria)

G: Absence of remarkable soiling of tube body

NG: Remarkable soiling of tube body

5 **[0104]**

5. Measurement of Glossiness

Glossiness on the front side of the laminates for tubes was measured in accordance with JIS K 7105 using the GM-3D Gloss Meter manufactured by Murakami Color Research Laboratory Co., Ltd.

10 **[0105]**

6. Sensory Evaluation of Texture and Gloss

The front sides of the laminates for tubes were touched by hand while also visually observing under fluorescent light followed by evaluating in accordance with the criteria indicated below.

(Criteria)

VG: Moist texture and no reflection of fluorescent light

20 G: Soft texture and slight reflection of fluorescent light

NG: Slippery texture and formation of an outline of reflected fluorescent light

[0106]

25 The evaluation results of the laminates for tubes are shown in the following Table 2.

[0107]

[Table 2]

	Dry Laminate		Varnish Coating				
	Laminate Strength (N/15mm)		Coated amount (g/m ²)	Destaticizing properties	Soiling	Glossiness (%)	Sensory evaluation of texture and gloss
	Initial	After aging					
Example 1	7	15	1.5	G	G	60	NG
Example 2	7	15	1.5	NG	NG	11	VG
Example 3	7	15	1.5	G	G	11	G
Comp.Ex.1	7	15		NG	NG	68	NG
Comp.Ex.2	Unconfirmed	3		NG	NG	65	NG

30 **[0108]**

[Tables 1 and 2]

Based on a comparison of Examples 1 to 3 with Comparative Example 1, when a varnish containing an antistatic agent and/or matting agent was coated onto the front side of the surface layer, it was determined that laminate strength between the surface layer and ink layer can be secured while imparting antistatic properties and/or a matte finish to the laminates for tubes without the antistatic agent and/or matting agent having an effect on the adhesive layer.

10 **[0109]**

In addition, since the ink-coated sides of Examples 1 to 3, in which UV ink was front-printed onto the polyolefin (LLDPE) side of the laminates for tubes, are more flexible in comparison with gravure plate back-printing onto a PET substrate (Comparative Example 2), cohesive peeling or surface layer separation attributable to relaxation of stress did not occur, and sufficient laminate strength was determined to be able to be secured even after aging.

20 **[0110]**

In Comparative Example 2, cohesive peeling of the ink layer or surface layer cleavage of the PET layer was observed following aging. Thus, the laminate for tubes of Comparative Example 2 is predicted to undergo surface layer separation when external force is applied to the end surface during formation of a shoulder portion and the like.

[0111]

Experiment 2: Reference Examination of Laminate for Tubes not having Functional Coating layer

30 **[0112]**

<Fabrication of Laminates for Tubes>

UV inks, adhesives and surface layers were prepared as indicated in the following Table 3 for Reference Examples 1 to 3 and Comparative Reference Example 1.

35 **[0113]**

[Table 3]

	Ref. Examples				Comp. Ref. Ex.
	1	2	3	4	1
UV ink	FDFL + 5% Add.	FDFL + 5% Add.	FDFL + 5% Add.	FDFL + 5% Add.	FDFL + 5% Add.
Adhesive	Two-component-type adhesive				
Main component	TM-277	TM-277	A-310	A-620	A969V
Curing agent	Cat-RT86	Cat-10L	A-3	A-65	A-8
Surface layer	L-103	L-103	L-103	L-103	L-103

[0114]

Explanation of Abbreviations in Table 3

5 FDFL: Trade name of UV-curable flexographic ink
(manufactured by Toyo Ink Co., Ltd.)

Add.: Hexamethylene diisocyanate

TM-277: Trade name of ester-based main component
(manufactured by Toyo-Morton, Ltd.)

10 A-310: Trade name of ester-based main component
(manufactured by Mitsui Chemicals, Inc.)

A-620: Trade name of ester-based main component
(manufactured by Mitsui Chemicals, Inc.)

A-969V: Trade name of ether-based main component
15 (manufactured by Mitsui Chemicals, Inc.)

Cat-RT86: Trade name of aliphatic curing agent
(manufactured by Toyo-Morton, Ltd.)

Cat-10L: Trade name of aromatic curing agent
(manufactured by Toyo-Morton, Ltd.)

20 A-3: Trade name of aromatic curing agent
(manufactured by Mitsui Chemicals, Inc.)

A-65: Trade name of aliphatic curing agent
(manufactured by Mitsui Chemicals, Inc.)

A-8: Trade name of aromatic curing agent
25 (manufactured by Mitsui Chemicals, Inc.)

L-103: Trade name of LLDPE film (manufactured by
Aicello Chemical Co., Ltd., thickness: 90 μm)

[0115]

A substrate having a width of 200 mm and length of
30 800 m was prepared having a layered structure of

LLDPE(50)/LDPE(80)/EAA(20)/AL(12)/EMAA(30)/PET(12)//LLDPE
(100) in that order moving from the front to the back
(numbers in parentheses represent thickness in μm units).

[0116]

5 UV ink was flexographically printed on the surface
of the substrate to form a printing layer.

[0117]

Laminates for tubes were obtained by dry-laminating
the printing layer and surface layer with an adhesive
10 interposed there between in accordance with the
production conditions indicated below using a dry
lamination apparatus.

(Production Conditions)

Line speed: 30 m/min

15 Adhesive coated amount: 3.5 g/m²

[0118]

The laminates for tubes of Reference Examples 1 to 4
and Comparative Reference Example 1 had a layered
structure of LLDPE(90)//printing layer-
20 LLDPE(50)/LDPE(80)/EAA(20)/
AL(12)EMAA(30)/PET(12)//LLDPE(100) in that order moving
from the front to back.

[0119]

In addition, a commercially available laminate for
25 tubes having a gravure printing layer was prepared for
use as Comparative Reference Example 2. This
commercially available laminate for tubes had a layered
structure of LLDPE(35)/LLDPE/LDPE(20)/PET-printing
layer/LDPE(25)/white LDPE(100)/PETSIO_x(12)/EMAA/LLDPE(80)
30 in that order moving from the front to the back.

[0120]

<Evaluation of Laminates for Tubes>

1. Measurement of Initial Laminate Strength between
Surface Layer (Polyolefin) and UV Ink Layer

35 Laminates for tubes were cut to a size measuring 15
mm wide and 150 mm long 30 minutes after fabricating the
laminates for tubes of Reference Examples 1 to 4 and

Comparative Reference Example 1 to obtain test pieces.

[0121]

Each of the test pieces was evaluated for initial laminate strength between the surface layer and UV ink layer in accordance with the following measurement conditions using Strograph (for E-L) manufactured by Toyo Seiki Kogyo Co., Ltd.

(Measurement Conditions)

Clamping width: 50 mm

Pulling speed: 150 mm/min

Type of peeling: T-peeling

[0122]

The results of measuring initial laminate strength are shown in the following Table 2.

[0123]

2. Measurement of Laminate Strength after Aging

The laminates for tubes of Reference Examples 1 to 4 and Comparative Reference Examples 1 and 2 were aging over the course of 6 days at 40°C.

[0124]

The aged laminates for tubes were cut to a size measuring 15 mm wide and 150 mm long to obtain test pieces.

[0125]

Laminate strength after aging was measured between the surface layer and UV ink layer for the test pieces of Reference Examples 1 to 4 and Comparative Reference Example 1 in accordance with the same measurement conditions as those used for initial laminate strength using Strograph (for E-L) manufactured by Toyo Seiki Kogyo Co., Ltd., while laminate strength after aging was measured between the printed surface of the PET-printing layer and the LDPE layer there beneath for the test piece of Comparative Example 2.

[0126]

The results of measuring laminate strength after aging are shown in the following Table 4.

[0127]

[Table 4]

	Adhesive		Laminate Strength (N/15 mm)	
	Main component	Curing agent (aliphatic/ aromatic)	Initial	After Aging
Reference Example 1	TM-277	Cat-RT86 (aliphatic)	7	16
Reference Example 2		Cat-10L (aromatic)	6	15
Reference Example 3	A-310	A-3 (aromatic)	7	15
Reference Example 4	A-620	A-65 (aliphatic)	7	14
Comp. Ref. Ex. 1	A-969V	A-8 (aromatic)	2	10
Comp. Ref. Ex. 2	Unconfirmed	Unconfirmed	Not measured	3

[0128]

5 [Initial Laminate Strength]

On the basis of Table 4, adequate laminate strength can be understood to be obtained even immediately after lamination in Reference Examples 1 to 4 using a polyester-based main component.

10 **[0129]**

On the other hand, in the case of Comparative Reference Example 1 using an ether-based main component, laminate flaking occurred when stress was applied to the laminate due to inadequate initial laminate strength. Thus, the laminate for tubes of Comparative Reference Example 1 had inadequate handling ease.

[0130]

[Laminate Strength after Aging]

20 On the basis of Table 4, Reference Examples 1 to 4, in which UV ink was surface-printed on the polyolefin (LLDPE) side of the substrate, can be understood to secure adequate laminate strength even after aging without causing cohesive peeling or surface layer peeling attributable to relaxation of stress since the ink-coated side is flexible in comparison with the gravure laminate back-printed on a PET substrate (Comparative Reference

Example 2).

[0131]

In Comparative Reference Example 2, cohesive peeling
of the ink layer or surface layer peeling of the PET was
5 observed after aging. Thus, the laminate for tubes of
Comparative Reference Example 2 is predicted to undergo
surface layer peeling when external force is applied to
the end surface such as when forming the shoulder portion
and the like.

10 BRIEF DESCRIPTION OF THE REFERENCE SYMBOLS

[0132]

- 1 Laminate for tubes
- 2 Front side
- 3 Back side
- 15 4 Adhesive layer
- 5 Ink layer
- 6 Polyethylene terephthalate layer
- 7 Low density polyethylene film containing
antistatic agent
- 20 8 Other layer or laminate
- 9 Extrusion laminate
- 10 Dry laminate
- 11 Anchoring agent layer
- 12 Polyethylene layer
- 25 13 Polypropylene layer
- 14 Laminate for tubes
- 15 Functional coating layer
- 16 Surface layer
- 16 Seal portion
- 30 17 Laminated substrate
- 17a Polyolefin Surface
- 17b Portion other than polyolefin surface

1. A laminate for tubes having a functional coating layer, a surface layer, an adhesive layer, an ink layer and a laminated substrate laminated in that order moving from the front to back, wherein the adhesive layer comprises a two-
5 component-type adhesive consisting of a polyol having an ester moiety and a polyisocyanate, the ink layer comprises UV ink, and the side of the laminated substrate that contacts the ink layer comprises a polyolefin and wherein the laminate can provide a tubular container in which the body portion thereof
10 is fully printed by surface printing.
2. The laminate for tubes according to claim 1, wherein the functional coating layer is a varnish containing a functional material coated onto the surface layer.
3. The laminate for tubes according to claim 2, wherein
15 the functional coating layer is not present at least a portion of a seal portion of the surface layer.
4. The laminate for tubes according to claim 2 or 3, wherein the functional material is an antistatic agent and/or matting agent.
- 20 5. The laminate for tubes according to any one of claims 1 to 4, wherein the surface layer contains a low-density polyethylene and/or linear low-density polyethylene.
6. The laminate for tubes according to any one of claims 1 to 5, wherein the surface layer contains a
25 polyethylene terephthalate film.
7. The laminate for tubes according to any one of claims 1 to 6, wherein the polyol having an ester moiety is a polyester polyol.
8. The laminate for tubes according to any one of
30 claims 1 to 6, wherein the UV ink contains a polyisocyanate.
9. The laminate for tubes according to any one of claims 1 to 6, wherein the UV ink is UV flexographic ink.
10. The laminate for tubes according to any one of claims 1 to 9, wherein the laminated substrate comprises a
35 polyethylene terephthalate film.

11. The laminate for tubes according to any one of claims 1 to 10, wherein the initial laminate strength between the surface layer and the ink layer is 3.0 N/15 mm or more.

5 12. The laminate for tubes according to any one of claims 1 to 11, wherein the ink layer is located on the surface of the laminated substrate at a location corresponding to a seal portion.

10 13. The laminate for tubes according to any one of claims 1 to 12, wherein the ink layer is located over the entire surface of the laminated substrate.

14. The laminate for tubes according to any one of claims 1 to 13, wherein the surface layer contains a polyolefin and the UV ink layer is located on the surface of the laminated substrate at a location corresponding to a seal portion.

15 15. A tubular container having a body portion formed with the laminate for tubes according to any one of claims 1 to 14.