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FORM 1

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

Kuraray Co., Ltd, of 1621, Sakazu, Kurashiki-City, JAPAN, hereby apply for the grant of a standard patent for an invention entitled:

Resin Composition and Multilayered Structure

which is described in the accompanying complete specification.

Details of basic application(s):-

<u>Basic Applic. No:</u>	<u>Country:</u>	<u>Application Date:</u>
61-310773	JAPAN	30 December 1986

The address for service is:-

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DATED this TWENTY THIRD day of DECEMBER 1987

Kuraray Co., Ltd

By: *M.J. Anderson*

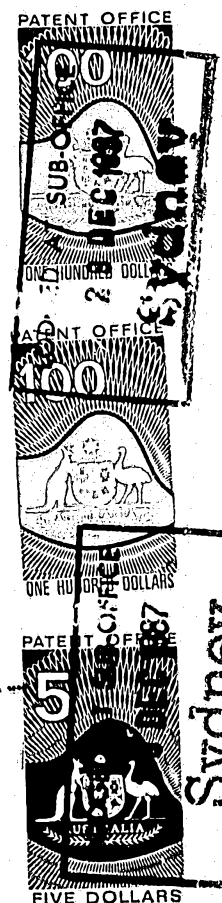
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Registered Patent Attorney

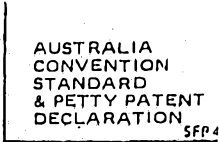
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 OUR REF: 46445
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COMMONWEALTH OF AUSTRALIA
THE PATENTS ACT 1952
DECLARATION IN SUPPORT OF A
CONVENTION APPLICATION FOR A PATENT



In support of the Convention Application made for a patent for an invention entitled:

Title of Invention

RESIN COMPOSITION AND MULTILAYERED STRUCTURE

Full name(s) and address(es) of Declarant(s)

I/We Tetuo Mizukami
of 3-11-11-210, Kaida, Nagaokakyo-City, Japan

do solemnly and sincerely declare as follows:-

Full name(s) of Applicant(s)

- 1. ~~I am/We are the applicant(s) for the patent~~
(or, in the case of an application by a body corporate)
- 1. I am/We are authorised by
KURARAY CO., LTD.
the applicant(s) for the patent to make this declaration on its/their behalf.
- 2. The basic application(s) as defined by Section 141 of the Act was/were made

Basic Country(ies)

in Japan

Priority Date(s)

on December 30, 1986

Basic Applicant(s)

by KURARAY CO., LTD.

Full name(s) and address(es) of inventor(s)

- 3. ~~I am/We are the actual inventor(s) of the invention referred to in the basic application(s)~~
(or where a person other than the inventor is the applicant)
- 3. Taichi Negi, Nobuo Tanaka and Kiyoshi Yonezu
of 131-1, Yasue, Kurashiki-City, Japan
11-23, Shishigaguchi-Cho, Nishinomiya-City, Japan and
1652, Sakazu, Kurashiki-City, Japan
(respectively)

is/are the actual inventor(s) of the invention and the facts upon which the applicant(s) is/are entitled to make the application are as follows:

Set out how Applicant(s) derive title from actual inventor(s) e.g. The Applicant(s) is/are the assignee(s) of the invention from the inventor(s)

The Applicant is the assignee of the invention from the inventors

- 4. The basic application(s) referred to in paragraph 2 of this Declaration was/were the first application(s) made in a Convention country in respect of the invention(s) the subject of the application.

Declared at Kurashiki- this 1st day of December 19 87
City

Tetuo Mizukami

Signature of Declarant(s)

(12) PATENT ABRIDGMENT (11) Document No. AU-B-83094/87
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(54) Title
RESIN COMPOSITION AND MULTILAYERED STRUCTURE

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(56) Prior Art Documents
AU 72931/87 B32B 27/08 C08L 23/08 23/04 C08K 3/32
AU 655779 10854/83 C08L 29/04 23/08 77/02 77/06 C08J 5/18

(57) Claim

1. A resin composition comprising 95 to 30 parts by weight of a saponified product of ethylene-vinyl acetate copolymer (A), containing ethylene units in an amount of 20 to 55 mole percent, and having a degree of saponification of the vinyl acetate component of at least 90 mole percent, and 5 to 70 parts by weight of a saponified product of modified ethylene-vinyl acetate copolymer (B) containing pyrrolidone ring containing units in an amount of 0.1 to 10 mole percent, and ethylene units in an amount 20 to 55 mole percent, and having a degree of saponification of the vinyl acetate component of at least 90 mole percent.

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4. A multilayered structure comprising a layer of the resin composition comprising of 95 to 30 parts by weight of a saponified product of ethylene-vinyl acetate copolymer (A) containing ethylene units in an amount of 20 to 55 mole percent, and having a degree of saponification of the vinyl component of at least 90 mole percent, and 5 to 70 parts by weight of a saponified product of modified ethylene-vinyl acetate copolymer (B) containing pyrrolidone ring-containing units in an amount of 0.1 to 10 mole percent, and ethylene units in an amount of 20 to 55 mole percent, and having a degree of saponification of the vinyl acetate component of at least 90 mole percent, and at least one layer of thermoplastic resin on the layer of the above mentioned resin composition.

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FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

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Complete Specification Lodged:

Accepted:

Published:

Priority:

Related Art:

This document contains the amendments made under Section 49 and is correct for printing.

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of Applicant:

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Complete Specification for the invention entitled:

Resin Composition and Multilayered Structure

The following statement is a full description of this invention, including the best method of performing it known to me/us

ABSTRACT OF THE DISCLOSURE

There is described a resin composition containing a saponified product of modified ethylene-vinyl acetate copolymer containing 0.1 to 10 mole percent of pyrrolidone ring containing units, and a formed article made of this composition especially a multilayered structure formed by a high speed theremodrawing, having excellent uniform gas barrier properties without pinholes, cracks, and localized uneven stretching.

TITLE OF THE INVENTION
RESIN COMPOSITION AND MULTILAYERED STRUCTURE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a saponified product of ethylene-vinyl acetate copolymer (referred to as EVOH hereinafter) composition, which is superior in thermdrawability without pinholes, cracks, localized uneven stretching and the like, and in gas barrier properties, and a multilayered structure utilizing this resin composition, especially thermdrawn, more particularly high speed thermdrawn multilayered structure.

2. Description of the Prior Art

EVOH resin is well noted for its effectiveness in the area of food packaging film, especially for the food requiring oxygen barrier packaging and other articles requiring aromaproofness. EVOH single layer film is poor

in toughness and has insufficient barrier properties to moisture and water.

For the improvement of these disadvantages, EVOH is often used in combination with thermoplastic resins such as polypropylene, polystyrene and the like, and heat sealing layers such as ionomer, ethylene-vinyl acetate copolymer and the like in the form of multilayered laminate structure.

10 When fabricated products such as containers and the like made of multilayered structures produced by various methods (films, sheets, parisons and the like), especially drawn formed under the melting point of EVOH, EVOH layer severely suffers in small voids, cracks, and localized uneven stretching, so that the oxygen barrier properties of the formed containers are greatly deteriorated. As the result, the formed containers cannot be used as packaging for food because of the poor appearance.

20 There have been proposed several methods for preventing pinholes, cracks and the like at the thermodrawing. According to Japanese Patent Laid-open Nos. 88,067/1978 and 20345/1984, various plasticizers are added to EVOH, and according to Japanese Patent Laid-open Nos. 141,785/1977, 154,755/1983 and 36,412/1983, EVOH resin is blended with polyamide resin, but the problems remain undissolved satisfactorily in the following points. That is, in the

case of addition of plasticizers containing hydroxyl group, aromatic sulfonamides and the like, this method cannot be put practical use because the addition of plasticizers in the desired range of 10 to 20 weight percent to EVOH greatly sacrifices the gas barrier properties, and also decreases the adhesive strength between EVOH layer and other plastic resin layers presumably because of the bleed of plasticizer.

10 On the other hand, a method which comprises blending polyamide resins with EVOH to impart flexibility thereto and improve fabricability is well known and many patent applications have been filed. (Japanese Patent Publication Nos. 24,277/1969, 24,813/1985, and 38,897/1979, Japanese Patent Laid-open Nos. 129,035/1983 and 36,412/1983.)
20 However, the blend of the polyamides being capable of improving high speed thermdrawability cannot be put to practical use because of forming a lot of gels in the formed articles presumably by the high reactivity of the polyamides with EVOH, and tinting remarkably. The blend of polyamide with EVOH being less tinting is also known in patents and gives good formed articles at a sight without apparent cracks, pinholes and localized uneven stretching at low speed thermdrawing, but gives big scattering of observed values of gas barrier properties estimated very small unobservable pinholes with the naked eye, presumably because of low

compatibility with EVOH. Furthermore, the recent speed up of thermodrawing machine causes the increase of scattering of observed values in gas barrier properties and the decrease of the reliability as gas barrier container.

10 The recent requirement for prolonged preservation period of packaged food demands the higher performance of packaging in gas barrier properties. The thickening of EVOH layer to meet these requirements tends to produce very small pinholes, cracks, localized uneven stretching and the like as compared with the case of rather thin EVOH layer in thermodrawing, increases the scattering of observed values of gas barrier properties and decreases the reliability as gas barrier container.

The tendency to blend scraps, such as trimmings at the formation, defect containers and the like to the thermoelastic resins for the decrease of product cost. In this case, the thermoplastic resin layer blended with the recovery plastic resins tends to have localized uneven stretching, cracks and the like, and to become a poor appearance.

20 The development of EVOH with excellent forming characteristics, giving superior gas barrier properties and highly reliable gas barrier containers (with less scattered observed values in gas barrier properties) without pinholes, cracks, localized uneven stretching and the like at the high speed thermodrawing.

SUMMARY OF THE INVENTION

EVOH resin has many superior characteristics as mentioned above, but also has some disadvantages liable to produce cracks, very small pinholes, localized uneven stretching and the like at the processing of a laminate structure with thermoplastic resin to container, which deteriorates the gas barrier properties. In this case, the appearance is also damaged and cannot be used as a food packaging container.

As the results of extensive studies, the present inventors accomplished this invention of EVOH new composition keeping the excellent gas barrier properties of EVOH and being capable of processing into a high barrier container of multilayered structure without producing cracks, pinholes, localized uneven stretching and the like.

It is an object of the present invention to provide a resin composition comprising 95 to 55 weight percent of saponified product of ethylene-vinyl acetate copolymer (referred to as EVOH(A) hereinafter) containing ethylene units in an amount of 20 to 55 mole percent and having a degree of saponification of the vinyl acetate component of at least 90 mole percent, and 5 to 45 weight percent of

saponified product of modified ethylene-vinyl acetate copolymer (referred to as EVOH(B) hereinafter) containing pyrrolidone ring containing units in an amount of 0.1 to 10 mole percent, ethylene units in an amount of 20 to 55 mole percent and having a degree of saponification of the vinyl acetate component of at least 90 mole percent, and a multilayered structure composed of a layer made of this resin composition with a thermoplastic resin layer on at least one side, particularly that of thermodrawn, more particularly that of high speed thermodrawn.

According to a first embodiment of this invention, there is provided a resin composition comprising 95 to 30 parts by weight of a saponified product of ethylene-vinyl acetate copolymer (A), containing ethylene units in an amount of 20 to 55 mole percent, and having a degree of saponification of the vinyl acetate component of at least 90 mole percent, and 5 to 70 parts by weight of a saponified product of modified ethylene-vinyl acetate copolymer (B) containing pyrrolidone ring containing units in an amount of 0.1 to 10 mole percent, and ethylene units in an amount 20 to 55 mole percent, and having a degree of saponification of the vinyl acetate component of at least 90 mole percent.

According to a second embodiment of this invention, there is provided a multilayered structure comprising a layer of the resin composition comprising of 95 to 30 parts by weight of a saponified product of ethylene-vinyl acetate copolymer (A) containing ethylene units in an amount of 20 to 55 mole percent, and having a degree of saponification of the vinyl component of at least 90 mole percent, and 5 to 70 parts by weight of a saponified product of modified ethylene-vinyl acetate copolymer (B) containing pyrrolidone ring-containing units in an amount of 0.1 to 10 mole percent, and ethylene units in an amount of 20 to 55 mole percent, and having a degree of saponification of the vinyl acetate component of at least 90 mole percent, and at least one layer of thermoplastic resin on the layer of the above mentioned resin composition.

EVOH(A) and EVOH(B) used in this invention contain ethylene units in an amount of 20 to 55 mole percent, preferably 25 to 50 mole percent, and have a degree of saponification of at least 90 mole percent, preferably at least 96 mole percent. With less than 20 mole percent of ethylene units, the formation of this resin becomes difficult because the formation temperature approaches the decomposition temperature. With more than 55 mole percent of ethylene units, the gas barrier properties of formed articles decreases and the multiple layer structure container using this formed article unpreferably suffers in inferior gas barrier properties. With less than 96 mole percent, especially less than 90 mole percent of



vinyl acetate units in the degree of saponification, EVOH resin can be formed in containers with few or more of cracks, pinholes and the like, but unpreferably suffers in inferior gas barrier properties. Further EVOH(A) and EVOH(B) have a melt index (observed by the method of ASTM-D 1238-65T, at 190°C under a load of 2160 g) of 0.1 to 25 g/10 minutes, preferably 0.3 to 20 g/10 minutes.

10 EVOH(B) should contain pyrrolidone ring-containing units in an amount of 0.1 to 10 mole percent, preferably 0.1 to 5 mole percent. With less than 0.1 mole percent of pyrrolidone ring-containing units, it does not provide good-looking formed articles free of cracks and localized uneven stretching on account of its insufficient improvement in drawability in the blending with EVOH(A). With more than 10 mole percent of pyrrolidone ring-containing units, it is poor in thermal stability and liable to gelation at the time of melt forming. In addition, it is low in water resistance and moisture resistance, which lead to poor gas barrier properties in a high humidity atmosphere.

20 suitable pyrrolidone ring-containing monomer is N-vinyl-2-pyrrolidone or a derivative thereof, the former being preferable. EVOH(B) is obtained by the saponification of the copolymer polymerized of ethylene, vinyl acetate and a pyrrolidone ring-containing monomer.

The ratio of mixture of EVOH(A) and EVOH(B) (referred

to as the ratio (A/B) hereinafter) is 95/5 to 30/70, preferably 95/5 to 55/45. With more than the ratio (A/B) of 95/5, it tends to produce cracks, pinholes; and localized uneven stretching at the formation of container, and unpreferably results in wide scattering of observed value of gas barrier properties. With less than the ratio (A/B) of 30/70, it becomes difficult to keep even thickness in film, especially in coextruded film.

it is preferable that

In this invention, EVOH(A) and EVOH(B) have ethylene units of more than 5 mole percent difference and preferably satisfy the following equations.

$$E'(B) \leq 10^9 \text{ dyne/cm}^2 \quad (\text{I})$$

$$1.0 \leq E'(A)/E'(B) \quad (\text{II})$$

$$|SP(A) - SP(B)| \geq 0.1 \quad (\text{III})$$

$$0.05 \leq MI(A)/MI(B) \leq 20 \quad (\text{IV})$$

wherein:

E'(A) is the dynamic viscoelasticity of EVOH(A) in dyne/cm² at thermodrawing formation temperature,

E'(B) is the dynamic viscoelasticity of EVOH(B) in dyne/cm² at thermodrawing formation temperature,

SP(A) is the solubility parameter of EVOH(A) (by Small method),

SP(B) is the solubility parameter of EVOH(B) (by Small method).

With less than 5 mole percent difference of EVOH(A)

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and EVOH(B) ethylene units, with more than 20 or less than 0.05 of the melt index ratio of EVOH(A) to EVOH(B) MI(A)/MI(B), or with less than 0.1 of solubility parameter difference of EVOH(A) and EVOH(B) $|SP(A) - SP(B)|$, it tends to produce cracks and pinholes at the formation of container, and results in wide scattering of observed value of gas barrier properties, presumably because of uneven dispersion of blending of EVOH(A) and EVOH(B). With more than 10^9 dyne/cm² of dynamic viscoelasticity of EVOH(B) at thermodrawing formation temperature $E'(B)$, or with less than 1.0 of the ratio of dynamic viscoelasticity of EVOH(A) to EVOH(B) at thermodrawing formation temperature $E'(A)/E'(B)$, it tends to become uneven drawing at container formation.

The blending process of EVOH(A) with EVOH(B) is not specifically limited but preferable examples include dry blending of EVOH(A) with EVOH(B), pelletizing and drying it by a bunbury mixer, single-screw or twin-screw extruder and the like.

When the blend is heterogeneous or gel and hard spots occur or contaminate upon the blending operation, it is highly likely that breakage of the EVOH blend layer and unevenness might often occur upon thermo drawing. Therefore, it is desired that an extruder having a high kneading degree be used, the opening of a hopper be sealed with $\frac{1}{2}$ and the extrusion be performed at low temperatures, upon blending with heating using an extruder.

Additives such as resins, anti-oxidants, plasticizers, and colorants may be added in the range of not disturbing the effect of the invention. Preferably heat stabilizers such as hydrotalcites, hindered phenols, hindered amines and the like are added in the range of 0.01 to 1 weight percent.

Although the EVOH composition of this invention can be formed in a film, sheet, tube, bottle and the like by a well known melt forming and compression forming, this composition can exhibit its features most effectively when used as one layer of the multilayered structure. The further details will be described in the following.

The thermoplastic resin to be used in the multilayered structure of this invention which can be formed under drawing in the following temperature range includes polypropylene, saturated polyester, polystyrene, polyamide, polyvinyl chloride. Preferable among them are polypropylene (homo polypropylene, ethylene-propylene bloc. copolymer, ethylene-propylene random copolymer and the like), polystyrene (homo styrene, high impact resistant grade polystyrene and the like) and saturated polyester.

When the melting point of EVOH and the temperature of the thermoplastic resin upon thermo drawing are designated $X^{\circ}\text{C}$ and $Y^{\circ}\text{C}$ respectively, the following equation must be satisfied:

$$X - 10^{\circ}\text{C} \geq Y \geq X - 110^{\circ}\text{C}$$

In the case of Y is higher than $(X-10)^{\circ}\text{C}$, EVOH can be formed without any particular additives because EVOH softens and melts at a temperature of this range. On the other hand, in the case of Y is lower than $(X-110)^{\circ}\text{C}$, the glass transition temperature (T_g) of the thermoplastic resin being under room temperature makes difficult the formed articles being in practical use because of the shape and dimension unstability in room temperature.

The process to get the multilayered structure of this invention comprises making the laminate of this EVOH composition and thermoplastic resin through adhesive resin by extrusion lamination, dry lamination, coextrusion lamination, coextrusion sheet formation (feed block or multiple manifold method), coextrusion pipe formation, coinjection, solutions coating method and the like, and stretching the heated laminate under the melting point of the thermoplastic resin with vacuum air-pressure deep draw former, biaxial stretch blow molder or the like (SPPF formation), thermodrawing the laminate (sheet or film) with biaxial stretcher, and coinjection biaxial stretching of EVOH composition with thermoplastic resin and the like.

As for the thickness construction of multilayered structure, the tensile force ratio of EVOH layer to thermoplastic resin layer is 5 or less, preferably 1 or less. With more than 5 of tensile force ratio of EVOH

layer to thermoplastic resin layer, this EVOH composition is liable to produce unfavorable cracks and localized uneven stretching. The tensile force of thermoplastic resin layer in multilayered structure herein described is observed at 50 mm per minute of tensile rate, being 50 mm of chuck distance, at 100% elongation, at thermodraw formation temperature. The tensile force of EVOH is that of EVOH(A) EVOH(B) blended layer observed as described above.

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In case the tensile force of each layer is measured from a drawn multilayered structure, first the state of the draw of the drawn multilayered structure is turned back to the state of before drawing by hot-pressing a drawn multilayered structure, second the structure is separated into each layer and last the tensile force of each layer can be observed as described above.

20
The laminate may have the following structure. Thermoplastic resin layer/ EVOH composition layer/ thermoplastic resin layer, EVOH composition layer/ adhesive resin layer/ thermoplastic resin layer, thermoplastic resin layer/ adhesive resin layer/ EVOH composition layer/ adhesive resin layer/ thermoplastic resin layer are representatives. In the case of using thermoplastic resin layer on the both outer sides, they may be the same or different resin. The adhesive resin herein described is that can be drawn under the melting point of EVOH resin and be capable of adhering between EVOH composition layer and thermoplastic resin layer. The preferable examples are the polyolefine (such as polyethylene, polypropylene)

added or grafted ethylene unsaturated dicarboxylic acid or its anhydride (such as maleic anhydride), ethylene-vinyl acetate copolymer, ethylene-acrylate (such as methyl ester, ethyl ester) copolymer.

The thermodrawn multilayered structures herein described are the articles prepared by thermodrawing, such as containers containing cups, bottles and the like, sheet film type goods. Heating herein described means a method to heat this multilayered structure uniformly by keeping it at a satisfactory temperature for thermodrawing for a determined period. Uniform heating can be carried out preferably by various heaters at the stand point of operation. Heating may be carried out at the same time or before drawing. Drawing herein described means an operation to form an uniformly heated multilayered structure into a container, cup, sheet or film by chucks, plugs, vacuum air-pressure, blow or the like. An uniaxial or biaxial drawing (simultaneously or successive) can be employed. Draw ratio and draw rate of this invention may be selected appropriately for the purpose, but the high speed drawing described in this invention means the uniform formation of containers or film at the speed of more than 5×10^5 percent per minute and does not demanded the formed article to be oriented.

The draw ratio based on area should be 70 times or

less, preferably 3 to 60 times. With more than 70 times of draw ratio, the thermoplastic resin cannot be stretched uniformly, and the multilayered structure becomes poor.

The moisture content of EVOH composition layer, being one element of the multilayered structure, at the thermodrawing is not particularly limited, but preferably in the range of 0.01 to 10 percent.

The recovery of the trimming and scraps of defect containers and the like is not particularly limited. The scraps may be recovered by pulverizing, drying when moistured, and dryblending with thermoplastic resin of raw material; pelletizing and dryblending with thermoplastic resin of raw material; pulverizing, dryblending with thermoplastic resin, and pelletizing; and the like. As the blend ratio of scrap to thermoplastic resin of raw material is increased, localized uneven stretching, nonuniformity, cracks, haze and the like are liable to occur. Generally a blend ratio in the range of about 2 to 100 percent is acceptable. In this case plural additives such as maleic anhydride modified polyclefins, metal soap, hydrotalcite and the like are preferably added to improve the dispersibility and thermal stability, and to prevent unfavorable phenomena at the formation of container. Thus obtained high speed thermodrawn multilayered structure, having excellent gas barrier properties without pinholes,

cracks, and localized uneven stretching, is suitable for an uniform high quality packaging container for foods, aromaproof container and the like.

The invention is now described in more detail with reference to the following examples, which are not intended to limit the scope of the invention.

EXAMPLES

Example 1

EVOH(A) ("EP-E101", a product of Kuraray Co., Ltd.) containing ethylene units in an amount of 32 mole percent having 99.6 mole percent of degree of saponification, and 1.6 g/10 minutes of melt index (MI(A), at 190°C) was found to have 10.6 of solubility parameter SP(A) and 7×10^9 dyne/cm² of dynamic viscoelasticity E'(A) (at 130°C, 110 Hz) observed by Vibron (manufactured by Toyo Baldwin Co., Ltd.). EVOH(B) containing N-vinyl-2-pyrrolidone unit in an amount of 2 mole percent and ethylene units in an amount of 44 mole percent, having 5.5 g/10 minutes of melt index (MI(B) at 190°C) was found to have 9.8 of solubility parameter SP(B) and 6×10^8 dyne/cm² of dynamic viscoelasticity E'(B) (at 130°C). From these data, the

difference between SP(A) and SP(B) is 0.8, and the ratio of E'(A) to E'(B) ($E'(A)/E'(B)$) is 13. The blend of EVOH(A) and EVOH(B) containing 80 weight parts of EVOH(A) and 20 weight parts of EVOH(B) was pelletized by twin-screw type vented 40 ϕ extruder sealed the hopper opening with nitrogen gas at 200°C. The obtained pellets were dried at 80°C for 8 hours. The pellets were feeded to feed block type coextruder forming 5 layers with 3 extrudates. The obtained sheet was constituted with 800 μ of both outer layers made of polystyrene (PS) ("Idemitsu Styrol ET-61", a product of Idemitsu Petrochemical Co., Ltd.), 50 μ of adhesive layers made of maleic anhydride-modified ethylene-vinyl acetate copolymer ("Merthene M-5420", a product of Toyo Soda Mfg. Co., Ltd.), and 50 μ of inter layer made of the above mentioned EVOH. The tensile force of polystyrene (PS) layer of this sheet was 1.0 kg/15 mm width at 100% elongation at 130°C, and that of EVOH layer (50 μ) was 0.3 kg/15 mm width at the same condition, and the tensile force ratio of EVOH layer to PS layer, EVOH/PS becomes 0.3. This sheet was thermoformed by thermodrawing at 130°C by vacuum air-pressure former (at 9 x 10 percent/minute of draw rate, 1 of draw ratio, 7 times of stretch ratio). The obtained formed articles were excellent in clarity and appearance without cracks and localized uneven stretching. The gas barrier properties of this con-

tainer at 20°C, 65% RH (measured by 10/50 type of Mocon Co., Ltd.) was excellent as 0.7 cc. 20 μ /m² .24 hr.atm. and R(maximum value - minimum value, when n=20) was 0.2.

Comparative Example 1

In Comparative Example 1, the formed article was produced in the same manner as Example 1 using EVOH(B) containing ethylene units in an amount of 44 mole percent and having 99.4 mole percent of degree of saponification instead. The obtained formed containers cannot be in practical use in appearance because of being a lot of localized uneven stretching.

Example 2

The blend of EVOH(A) and EVOH(B) prepared in the same manner as Example 1 was formed into the bottle of 3 layers with 2 extrudates, constructing polyester ([η]=0.7)/blend of EVOH(A) and EVOH(B)/ polyester ([η]=0.7) by a coinjection costretch blow former manufactured by Nissei ASB Machine Co., Ltd. The dynamic viscoelasticity of EVOH(A), E'(A) at 100°C was 9 x 10⁹ dyne/cm², and that of EVOH(B), E'(B) at 100°C was 9 x 10⁸ dyne/cm². The tensile force of polyester layer of parison before

thermodrawing at 100°C was 3 kg/15 mm width, and that of EVOH layer was 0.4 kg/15 mm width. The ratio of tensile force of EVOH layer to polyester layer was 0.13. The gas barrier properties of the obtained bottle was excellent as 0.5 cc.20 μ /m² .24hr.atm. and R=0.1 without longitudinal stripes of localized uneven thickness, uneven stretching, cracks and the like.

Comparative Example 2

In Comparative Example 2, the formed bottle was produced in the same manner as Example 2 using EVOH(A) alone instead of the blend of EVOH(A) and EVOH(B). The obtained bottle cannot be in practical use in appearance because of a lot of longitudinal stripes of uneven thickness and localized uneven stretching.

Example 3

EVOH(A) containing ethylene units in an amount of 32 mole percent and having 99.6% of degree of saponification, and 1.5 g/10 minutes of melt index (MI(A), at 190°C) was found to have 10.6 of solubility parameter SP(A) and 20 3×10^9 dyne/cm² of dynamic viscoelasticity E' (A) (at 150°C). EVOH(B) containing N-vinyl-2-pyrrolidone units

in an amount of 1 mole percent and ethylene units in an amount of 40%, and having 5.0 g/10 minutes of melt index (MI(B), at 190°C) was found to have 10.0 of solubility parameter SP(B) and 1×10^8 dyne/cm² of dynamic viscoelasticity E'(B) (at 150°C). From these data, the difference between SP(A) and SP(B) is 0.6, and the ratio of E'(A) to E'(B) (E'(A)/E'(B)) is 30.

The blend of EVOH(A) and EVOH(B) containing 10 weight parts of EVOH(A) and 80 weight parts of EVOH(B) was pelletized and formed in sheet as the same manner of Example 1. The obtained sheet was constituted with 800 μ of both outer layers made of polypropylene ("Mitsubishi Noblen MA6", a product of Mitsubishi Petrochemical Co., Ltd.), 50 μ of adhesive layer made of maleic anhydride modified ethylene-vinyl acetate copolymer ("Admer QF500", a product of Mitsui Petrochemical Co., Ltd.), and 50 μ of inter layer made of the above mentioned EVOH.

The tensile force of polypropylene of this sheet was 1.6 kg/15 mm width at 150 °C, therefore the tensile force ratio of EVOH layer to polypropylene layer EVOH layer/polypropylene layer becomes 0.13.

This sheet was thermoformed by thermodrawing at 150°C by vacuum air-pressure former (at 9×10^5 percent/minute of draw rate, 1 of draw ratio, 7 times of stretch ratio.) The obtained formed articles were excellent in clarity and

appearance without cracks and localized uneven stretching.

The gas barrier properties of this container at 20°C, 65% RH was excellent as 0.6 cc.20 μ /m² .24hr.atm. and R(when n=20) was 0.2.

Example 4

In Example 4, the formed article was produced in the same manner as Example 3, using EVOH(A) containing ethylene units in an amount of 36 mole percent and having 99.6 mole percent of degree of saponification, and 1.5 g/10 minutes of melt index (MI, at 190°C) instead. EVOH(A) of this Example 4 was found to be 10.3 of solubility parameter, and 2×10^{10} dyne/cm² of dynamic viscoelasticity.

The obtained container can be in practical use with a little nonuniformity.

Example 5

The trimings and scraps of multilayered structure generated at the forming in Example 3 was pulverized and pelletized. The obtained pellets was blended with polypropylene resin (MA6) in an amount of 30 weight percent, and the obtained blended resin was formed in the same

manner as Example 3. The formed article was excellent container without cracks, nonuniformity, even though the recovered substances, such as trimings, scraps and the like were blended in the polypropylene layer. The tensile force ratio of EVOH layer to polypropylene layer, EVOH layer/ polypropylene layer was 0.15. The gas barrier properties of this container was excellent as 0.7 cc. $20 \mu / m^2$.24 hr. atm. of oxygen permeability and its R was 0.1.

~~What is claimed is~~ The claims defining the invention are as follows:

1. A resin composition comprising 95 to 30 parts by weight of a saponified product of ethylene-vinyl acetate copolymer (A), containing ethylene units in an amount of 20 to 55 mole percent, and having a degree of saponification of the vinyl acetate component of at least 90 mole percent, and 5 to 70 parts by weight of a saponified product of modified ethylene-vinyl acetate copolymer (B) containing pyrrolidone ring containing units in an amount of 0.1 to 10 mole percent, and ethylene units in an amount 20 to 55 mole percent, and having a degree of saponification of the vinyl acetate component of at least 90 mole percent.

2. A resin composition as described in Claim 1, wherein the pyrrolidone ring containing unit is N-vinyl-2-pyrrolidone.

3. A resin composition as described in Claim 1 or 2 wherein the difference of ethylene units of (A) and (B) ^{is} ~~being~~ at least 5 mole percent.

4. A multilayered structure comprising a layer of the resin composition comprising of 95 to 30 parts by weight of a saponified product of ethylene-vinyl acetate copolymer (A) containing ethylene units in an amount of 20 to 55 mole percent, and having a degree of saponification of the vinyl component of at least 90 mole percent, and 5 to 70 parts by weight of a saponified product of modified ethylene-vinyl



acetate copolymer (B) containing pyrrolidone ring-containing units in an amount of 0.1 to 10 mole percent, and ethylene units in an amount of 20 to 55 mole percent, and having a degree of saponification of the vinyl acetate component of at least 90 mole percent, and at least one layer of thermoplastic resin on the layer of the above mentioned resin composition.

5. A resin composition substantially as hereinbefore described with reference to any one of the Examples.

6. A multilayered structure substantially as hereinbefore described with reference to any one of the Examples.

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