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<p>(21) International Application Number: PCT/JP00/01644</p> <p>(22) International Filing Date: 17 March 2000 (17.03.00)</p> <p>(30) Priority Data:</p> <table border="0"> <tr> <td>11/73833</td> <td>18 March 1999 (18.03.99)</td> <td>JP</td> </tr> <tr> <td>11/73834</td> <td>18 March 1999 (18.03.99)</td> <td>JP</td> </tr> </table> <p>(71) Applicant (for all designated States except US): TEIJIN LIMITED [JP/JP]; 6-7, Minamihommachi 1-chome, Chuo-ku, Osaka-shi, Osaka 541-0054 (JP).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): YOSHIDA, Yoichi [JP/JP]; Teijin Limited, Matsuyama Factory, 77, Kitayoshida-cho, Matsuyama-shi, Ehime 791-8041 (JP). SUZUKI, Minoru [JP/JP]; Teijin Limited, Matsuyama Factory, 77, Kitayoshida-cho, Matsuyama-shi, Ehime 791-8041 (JP). NAGANO, Hiroki [JP/JP]; Teijin Limited, Matsuyama Factory, 77, Kitayoshida-cho, Matsuyama-shi, Ehime 791-8041 (JP).</p> <p>(74) Agent: OHSHIMA, Masataka; Ohshima Patent Office, Fukuya Building, 3, Yotsuya 4-chome, Shinjuku-ku, Tokyo 160-0004 (JP).</p>		11/73833	18 March 1999 (18.03.99)	JP	11/73834	18 March 1999 (18.03.99)	JP	<p>(81) Designated States: AE, AL, AU, BA, BB, BG, BR, CA, CN, CR, CU, CZ, DM, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MA, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>Without international search report and to be republished upon receipt of that report.</i></p>
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<p>(54) Title: HOLLOW MOLDED PRODUCT COMPRISING ETHYLENE-2,6-NAPHTHALENE DICARBOXYLATE POLYMER AND PRODUCTION PROCESS THEREFOR</p>								
<p>(57) Abstract</p> <p>A hollow molded product which contains a polyester composition containing an ethylene-2,6-naphthalene dicarboxylate polymer and at least one ultraviolet absorber in an amount of 0.01 to 5.0 wt% based on the ethylene-2,6-naphthalene dicarboxylate polymer, and which has a birefringence factor (Δn) of the barrel portion of 0.17 or more, and a process for preparation thereof.</p>								

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DESCRIPTION

HOLLOW MOLDED PRODUCT COMPRISING ETHYLENE-2,6-NAPHTHALENE
DICARBOXYLATE POLYMER AND PRODUCTION PROCESS THEREFOR

5

Field of the Invention

The present invention relates to a hollow molded product comprising an ethylene-2,6-naphthalene dicarboxylate polymer and to a production process therefor.

10 More specifically, it relates to a hollow molded product which comprises the above material and excellent in light resistance, resistance to an alkali aqueous solution, color and transparency and to a production process therefor.

Prior Art

15 When polyester containers which have been filled with a drink such as water, carbonated drink, beer or wine and shipped are collected and re-used while retaining their shapes. The collected containers are generally washed with an alkaline aqueous solution such as sodium hydroxide. For
20 example, polyethylene terephthalate containers are collected from the market, washed with an alkali, filled with a drink again and shipped to the market. They may be collected and recycled around 10 times. This number of recycling times is determined by the mechanical properties of the container,
25 the existence and degree of external scratches, the deterioration of the polymer and the like. The deterioration is caused by ultraviolet radiation when the polymer is exposed to the sunlight and by washing with an alkali. Deterioration by ultraviolet radiation or alkali is not called to account
30 and does not become marked when the polyethylene terephthalate container is collected and recycled about 10 times.

Since polyethylene naphthalate has excellent basic physical properties such as heat resistance, gas barrier

properties, chemical resistance and the non-adsorbability of contents and easily obtains high strength compared with polyethylene terephthalate, it has recently attracted much attention as a raw material for returnable bottles which can be used repeatedly, particularly bottles which can be re-used many times.

It has been found in the development of a returnable bottle of polyethylene naphthalate that the transparency of the bottle is reduced by washing a collected polyethylene naphthalate bottle with an alkali, for example, an aqueous solution containing 1 to 6 % of sodium hydroxide heated at 50 to 95°C. It has also been found that this reduction in transparency becomes larger as the number of times of recycling a polyethylene naphthalate bottle collected from the market by washing with an alkali solution increases.

A polyethylene naphthalate container is generally produced by injection molding a polymer obtained through a reaction in the presence of the same catalyst as that of polyethylene terephthalate to form a preform and then blow molding the preform.

However, since polyethylene naphthalate which is the raw material polymer of the container has higher melt viscosity and must be melt molded at a higher temperature than polyethylene terephthalate, the preform and the container are readily yellowed.

Although polyethylene naphthalate can absorb ultraviolet radiation itself, this characteristic property may not be sufficient to completely protect the contents of the container. That is, when a polyethylene naphthalate container is filled with a drink which is deteriorated by visible radiation having a wavelength of 400 to 500 nm, the above visible radiation cannot be shielded with polyethylene naphthalate which can absorb ultraviolet radiation having a wavelength of 380 nm or less. Therefore, it cannot be said

that polyethylene naphthalate is satisfactory in terms of the protection of the contents.

Disclosure of the Invention

5 It is an object of the present invention to provide a hollow molded product comprising ethylene-2,6-naphthalene dicarboxylate which does not cause a reduction in transparency even when the hollow molded product is exposed to ultraviolet radiation and washed with an alkali repeatedly
10 through its repeated use.

It is another object of the present invention to provide a hollow molded product comprising ethylene-2,6-naphthalene dicarboxylate which is excellent in color and transparency.

15 It is still another object of the present invention to provide a preform for producing the above hollow molded product of the present invention.

It is a further object of the present invention to provide an industrially advantageous process for producing the above hollow molded product of the present invention.

20 Other objects and advantages of the present invention will become apparent from the following description.

Summary of the Invention

25 According to the present invention, firstly, the above objects and advantages of the present invention are attained by a hollow molded product (may be referred to as "first hollow molded product of the present invention" hereinafter) (A1) which comprises a polyester composition comprising an ethylene-2,6-naphthalene dicarboxylate polymer which has
30 2,6-naphthalenedicarboxylic acid component in an amount of at least 80 mol% based on the total of all the dicarboxylic acid components and ethylene glycol component in an amount of at least 80 mol% based on the total of all the glycol components, and at least one ultraviolet absorber selected

from the group consisting of a benzotriazole compound, triazine compound, benzophenone compound, cyanoacrylate compound and benzooxazinone compound in an amount of 0.01 to 5.0 wt% based on the ethylene-2,6-naphthalene dicarboxylate polymer, and (B1) which has a birefringence factor (Δn) of the barrel portion of 0.17 or more.

Secondly, the above objects and advantages of the present invention are attained by a hollow molded product (may be referred to as "first laminate hollow molded product of the present invention" hereinafter) which has a laminate structure consisting of an outer layer of the polyester composition specified in (A1) above and an inner layer of an ethylene-2,6-naphthalene dicarboxylate polymer which does not contain an ultraviolet absorber or contains at least one ultraviolet absorber selected from the group consisting of the ultraviolet absorbers specified in (A1) above, and which has a birefringence factor of the barrel portion of 0.17 or more.

Thirdly, the above objects and advantages of the present invention are attained by a preform for producing the above first laminate hollow molded product and the first laminate hollow molded product of the present invention.

In the fourth place, the above objects and advantages of the present invention are attained by a hollow molded product (may be referred to as "second hollow molded product of the present invention" hereinafter) (A2) which comprises a polyester composition comprising an ethylene-2,6-naphthalene dicarboxylate polymer which has 2,6-naphthalenedicarboxylic acid component in an amount of at least 80 mol% based on the total of all the dicarboxylic acid components and ethylene glycol component in an amount of at least 80 mol% based on the total of all the glycol components, and at least one pigment selected from the group consisting of an oxide pigment, ferrocyanide pigment, silicate pigment,

phosphate pigment, carbon black, condensation polycyclic pigment and phthalocyanine pigment in an amount of 10 to 2,000 ppm, and (B2) which has a haze of the barrel portion of 10 % or less.

5 In the fifth place, the above objects and advantages of the present invention are attained by a preform for producing the above second hollow molded product of the present invention.

10 In the sixth place, the above objects and advantages of the present invention are attained by a hollow molded product (may be referred to as "third hollow molded product of the present invention" hereinafter) (A3) which comprises a polyester composition comprising an ethylene-2,6-naphthalene dicarboxylate polymer which has 2,6-
15 naphthalenedicarboxylic acid component in an amount of at least 80 mol% based on the total of all the dicarboxylic acid components and ethylene glycol component in an amount of at least 80 mol% based on the total of all the glycol components, at least one ultraviolet absorber selected from the group
20 consisting of a benzotriazole compound, triazine compound, benzophenone compound, cyanoacrylate compound and benzooxazinone compound in an amount of 0.01 to 5.0 wt% based on the ethylene-2,6-naphthalene dicarboxylate polymer, and at least one pigment selected from the group consisting of
25 an oxide pigment, ferrocyanide pigment, silicate pigment, phosphate pigment, carbon black, condensation polycyclic pigment and phthalocyanine pigment in an amount of 10 to 2,000 ppm, (B3) which has a birefringence factor (Δn) of the barrel portion of 0.17 or more and (B4) which has a haze of the barrel
30 portion of 10 % or less.

In the seventh place, the above objects and advantages of the present invention are attained by a process for producing a hollow molded product (may be referred to as "first production process of the present invention"

hereinafter) which comprises the steps of:

- (1) dry blending an ethylene-2,6-naphthalene dicarboxylate polymer which has 2,6-naphthalenedicarboxylic acid component in an amount of at least 80 mol% based on the total of all the dicarboxylic acid components and ethylene glycol component in an amount of at least 80 mol% based on the total of all the glycol components with at least one ultraviolet absorber selected from the group consisting of a benzotriazole compound, triazine compound, benzophenone compound, cyanoacrylate compound and benzooxazinone compound in an amount of 0.01 to 5.0 wt% based on the ethylene-2,6-naphthalene dicarboxylate polymer, or dry blending the above ethylene-2,6-naphthalene dicarboxylate polymer with a master polymer which contains both the above ethylene-2,6-naphthalene dicarboxylate polymer and at least one of the above ultraviolet absorbers in an amount of 1 to 10 wt% based on the ethylene-2,6-naphthalene dicarboxylate polymer to ensure that the content of the ultraviolet absorber should become 0.01 to 5.0 wt% based on the ethylene-2,6-naphthalene dicarboxylate polymer;
- (2) melt molding the obtained dry blend into a preform; and
- (3) blow molding the obtained preform into a hollow molded product having a birefringence factor of the barrel portion of 0.17 or more.

In the eighth place, the above objects and advantages of the present invention are attained by a process for producing a hollow molded product (may be referred to as "second production process of the present invention" hereinafter) comprising the steps of:

- (1) dry blending an ethylene-2,6-naphthalene dicarboxylate polymer which has 2,6-naphthalenedicarboxylic acid component in an amount of at least 80 mol% based on the total of all the dicarboxylic acid components and ethylene glycol component in an amount of at least 80 mol% based on

the total of all the glycol components with at least one pigment selected from the group consisting of an oxide pigment, ferrocyanide pigment, silicate pigment, phosphate pigment, carbon black, condensation polycyclic pigment and phthalocyanine pigment in an amount of 10 to 2,000 ppm, or dry blending the above ethylene-2,6-naphthalene dicarboxylate polymer with a master polymer which contains both the above ethylene-2,6-naphthalene dicarboxylate polymer and at least one of the above pigments in an amount of 0.01 to 1.0 wt% based on the ethylene-2,6-naphthalene dicarboxylate polymer to ensure that the content of the pigment should become 10 to 2,000 ppm;

(2) melt molding the obtained dry blend into a preform; and

(3) blow molding the obtained preform into a hollow molded product having a haze of the barrel portion of 10 % or less.

Detailed Description of the Invention

The first hollow molded product and the first laminate hollow molded product of the present invention are attained based on the finding that the exterior surface of a polyethylene naphthalate bottle is deteriorated by ultraviolet radiation while it is circulated in the market or stored after collection, a deteriorated portion is easily peeled off by washing with an alkali, and deterioration and peel-off become marked by repeating this cycle, thereby reducing the transparency of the bottle.

A description is first given of the first hollow molded product of the present invention.

The ethylene-2,6-naphthalate dicarboxylate polymer in the present invention is a polymer which contains 2,6-naphthalenedicarboxylic acid component in an amount of at least 80 mol% based on the total of all the acid components and ethylene glycol component in an amount of at least 80 mol% based on the total of all the glycol components. Other

acid components which can be copolymerized in an amount of less than 20 mol% include aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, phenylindanedicarboxylic acid, diphenoxyethanedicarboxylic acid, diphenylsulfonedicarboxylic acid, diphenyldicarboxylic acid, diphenyl ether dicarboxylic acid, 2,7-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid and 1,7-naphthalenedicarboxylic acid; aliphatic dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, adipic acid, azelaic acid and sebacic acid; alicyclic dicarboxylic acids such as cyclohexanedicarboxylic acid, decalindicarboxylic acid and tetralindicarboxylic acid; oxyacids such as glycolic acid and p-oxybenzoic acid. The acid components may be formed by using an acid and/or an ester forming derivative, particularly a lower alkyl ester in the production reaction of the ethylene-2,6-naphthalene dicarboxylate polymer. Preferred examples of the lower alkyl ester include dimethyl esters, diethyl esters and dipropyl esters. Out of these, dimethyl esters are preferred. When the acid component to be copolymerized is contained in the polymer in an amount of 20 mol% or more, the heat resistance and crystallinity of a bottle obtained from the polymer lower.

The ethylene-2,6-naphthalene dicarboxylate polymer in the present invention must have ethylene glycol in an amount of at least 80 mol% based on the total of all the glycol components. Other glycol components which can be copolymerized in an amount of less than 20 mol% include diethylene glycol, dimethylene glycol, trimethylene glycol, tetramethylene glycol, hexamethylene glycol, triethylene glycol, neopentyl glycol, cyclohexane dimethanol, bisphenol A and the like. Out of these, cyclohexane dimethanol and neopentyl glycol are preferred. When the glycol component to be copolymerized is contained in the polymer in an amount

of 20 mol% or more, the heat resistance and crystallinity of a bottle obtained from the polymer lower.

The total amount of the dicarboxylic acid component and the glycol component to be copolymerized in the present invention is preferably less than 20 mol%. When the total amount of the copolymerized components is 20 mol% or more, the heat resistance and crystallinity of the obtained polymer lower.

The method of producing the ethylene-2,6-naphthalene dicarboxylate polymer in the present invention is not limited to a direct esterification method and an ester exchange method, and the ester exchange reaction catalyst and the polycondensation reaction catalyst used are not limited to particular kinds as well. The catalysts are metal compounds which are widely known as an ester exchange reaction catalyst and a polycondensation reaction catalyst for polyethylene terephthalate. Examples of the ester exchange reaction catalyst include manganese compounds, calcium compounds, magnesium compounds, titanium compounds, zinc compounds, sodium compounds, potassium compounds, cerium compounds, lithium compounds, cobalt compounds and the like. Examples of the polycondensation reaction catalyst include titanium compounds, antimony compounds, germanium compounds and the like.

The ethylene-2,6-naphthalene dicarboxylate polymer produced by the ester exchange method and/or direct esterification method preferably contains a phosphorus compound as a stabilizer. The phosphorus compound is preferably phosphoric acid, phosphorous acid, hypophosphorous acid, phosphoric acid ester, phosphoric acid triester or the like.

The intrinsic viscosity (mixed solvent of 2 parts by weight of tetrachloroethane and 3 parts by weight of a phenol, 35° C) of the ethylene-2,6-naphthalene dicarboxylate polymer

is preferably 0.50 or more, more preferably 0.55 or more. This upper limit which depends on the characteristic properties and moldability of the container is preferably 0.80, more preferably 0.75.

5 Adding to the above polyethylene-2,6-naphthalene dicarboxylate polymer the polyester composition (A1) forming the first hollow molded product of the present invention contains at least one ultraviolet absorber selected from the group consisting of a benzotriazole compound, triazine
10 compound, benzophenone compound, cyanoacrylate compound and benzooxazinone compound in an amount of 0.01 to 5.0 wt%.

Examples of the benzotriazole compound include 2-(2H-benzotriazol-2-yl)-4-methylphenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol,
15 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)phenol, 2-(5-chloro-2H-benzotriazol-2-yl)-6-(1,1-dimethylethyl-4-methyl)phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylpropyl)phenol, 2,2'-methylenebis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol and 2-(2H-benzotriazol-2-yl)-6-dodecyl-4-methylphenol. Out of these, 2-(2H-benzotriazol-2-yl)-4-methylphenyl and 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol are preferred.
20 25

Examples of the triazine compound include 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyloxy)phenol, 2-(4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl)-5-(octyloxy)phenol, and 1,5,8,12-tetrakis(4,6-bis(N-butyl-N-1,2,2,6,6-pentamethyl-4-piperidylamino)-1,3,5-triazin-2-yl)-1,5,8,12-tetraazododecane. Out of these, 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyloxy)phenol is preferred.

Examples of the benzophenone compound include 2-

hydroxy-4-methoxy-5-sulfobenzophenone, 2-hydroxy-4-n-octoxybenzophenone, 2,4-dihydroxybenzophenone and 2-hydroxy-4-methoxybenzophenone.

Examples of the cyanoacrylate compound include 2-ethylhexyl-2-cyano-3,3'-diphenylacrylate and 2-ethyl-2-cyano-3,3'-diphenylacrylate.

Examples of the benzooxazinone compound include 2-p-methoxyphenyl(3,1-benzooxazin-4-one), 2- α -naphthyl(3,1-benzooxazin-4-one), 2- β -naphthyl(3,1-benzooxazin-4-one), 2-p-phthalimidephenyl(3,1-benzooxazin-4-one), 2,2'-bis(3,1-benzooxazin-4-one), 2,2'-p-phenylenebis(3,1-benzooxazin-4-one), 2,2'-(4,4'-diphenylene)bis(3,1-benzooxazin-4-one), 2,2'-(2,6- or 1,5-naphthalene)bis(3,1-benzooxazin-4-one) and 1,3,5-tris(3,1-benzooxazin-4-on-2-yl)benzene. Out of these, 2,2'-bis(3,1-benzooxazin-4-one) and 2,2'-p-phenylenebis(3,1-benzooxazin-4-one) are preferred.

These ultraviolet absorbers may be used alone or in combination of two or more. The amount of the ultraviolet absorber must be 0.01 to 5.0 wt%, preferably 0.05 to 1.5 wt% based on the ethylene-2,6-naphthalene dicarboxylate polymer. When the amount is smaller than 0.01 wt%, the ultraviolet light absorption of the ultraviolet absorber is small, thereby increasing the ultraviolet light absorption of the ethylene-2,6-naphthalene dicarboxylate polymer with the result of a great reduction in the transparency of a hollow molded product. When the amount is larger than 5.0 wt%, ultraviolet light absorptivity can be retained and a reduction in the transparency of the ethylene-2,6-naphthalene dicarboxylate polymer can be prevented but the discoloration of the ethylene-2,6-naphthalene dicarboxylate polymer becomes marked by adding the compound, thereby deteriorating the appearance of the obtained hollow molded product. Therefore, the above amount is not preferred from

the viewpoint of product value.

The hollow molded product made from the ethylene-2,6-naphthalene dicarboxylate polymer in the present invention must have a birefringence factor (Δn) of 0.17 or more. The measurement location of the birefringence factor (Δn) is almost the center of the barrel portion of the hollow molded product. This birefringence factor (Δn) can be obtained from a refractive index (n_{MD}) in the axial direction of the hollow molded product, a refractive index (n_{TD}) in the circumferential direction and a refractive index (n_Z) in the thickness direction according to the following equation (1).

$$\Delta n = \frac{n_{MD} + n_{TD}}{2} - n_Z \quad (1)$$

When this birefringence factor is smaller than 0.17, even if the hollow molded product made from the ethylene-2,6-naphthalene dicarboxylate polymer contains the above ultraviolet absorber, a reduction in the transparency of the hollow molded product caused by exposure to ultraviolet radiation and washing with an alkali which are carried out repeatedly is large.

The hollow molded product, for example, a bottle having the above birefringence factor can be obtained by stretching the barrel portion of a preform (pre-molded product of a bottle) to 3 times or more, preferably 5 times or more, more preferably 9 times or more in terms of area draw ratio at the time of blow molding. The thickness of the barrel portion is preferably 0.15 to 0.8 mm, more preferably 0.20 to 0.6 mm.

Preferably, the barrel portion of the hollow molded product made from the ethylene-2,6-naphthalene dicarboxylate polymer has a refractive index (n_Z) in the thickness direction of 1.54 or less. When the refractive index is more than 1.54, the plane orientation of the obtained

hollow molded product lowers disadvantageously.

The hollow molded product made from the ethylene-2,6-naphthalene dicarboxylate polymer in the present invention preferably has a haze of 15 % or less, more preferably 10 % or less after 15 times of repeated use. When the haze is more than 15 %, a reduction in transparency becomes marked, thereby reducing the product value of the hollow molded product.

Preferably, the hollow molded product made from the ethylene-2,6-naphthalene dicarboxylate polymer has a color b value (Col-b value) of 5 or less. When this b value is larger than 5, the hollow molded product deteriorates in color, thereby reducing the product value thereof.

Preferably, the hollow molded product made from the ethylene-2,6-naphthalene dicarboxylate polymer in the present invention has a carboxyl terminal group concentration of the polymer of 32 equivalents or less/ 10^6 g of the polymer. When the carboxyl terminal group concentration is higher than 32 equivalents/ 10^6 g of the polymer, the hollow molded product deteriorates in hydrolysis resistance under moist heat.

Preferably, the hollow molded product made from the ethylene-2,6-naphthalene dicarboxylate polymer in the present invention has an acetaldehyde content of the polymer of 30 ppm or less. When the acetaldehyde content is larger than 30 ppm and the hollow molded product is used as a food container, the hollow molded product deteriorates in flavor retention properties.

The hollow molded product made from the ethylene-2,6-naphthalene dicarboxylate polymer in the present invention may contain a hindered amine antioxidant. The content of this antioxidant is preferably 0.1 to 5.0 wt%.

Examples of the antioxidant include 1,5,8,12-tetrakis(4,6-bis(N-butyl-N-1,2,2,6,6-pentamethyl-4-

piperidylamino)-1,3,5-triazin-2-yl)-1,5,8,12-tetraazododecane, tetrakis(1,2,2,6,6-pentamethyl-4-piperidyl)1,2,3,4-butanetetracarboxylate, poly((6-((1,1,3,3-tetramethylbutyl)amino)-1,3,5-triazine-2,4-diyl)((2,2,6,6-tetramethyl-4-piperidyl)imino)hexamethylene((2,2,6,6-tetramethyl-4-piperidyl)imino)), 1,2,2,6,6-pentamethyl-4-piperidyl methacrylate, tetrakis (2,2,6,6-tetramethyl-4-piperidyl)1,2,3,4-butane tetracarboxylate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)-2-(3,5-di-t-butyl-4-hydroxybenzyl)-2-butyl malonate, bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate and 2,2,6,6-tetramethyl-4-piperidyl methacrylate.

15 A detailed description is subsequently given of the first laminate hollow molded product of the present invention.

The first laminate hollow molded product consists of an outer layer of the polyester composition (A) which
20 comprises an ethylene-2,6-naphthalene dicarboxylate polymer forming the first hollow molded product of the present invention and an ultraviolet absorber and an inner layer. The inner layer can be made from an ethylene-2,6-naphthalene dicarboxylate polymer containing no ultraviolet absorber or
25 an ethylene-2,6-naphthalene dicarboxylate polymer containing an ultraviolet absorber.

Since the polyester composition constituting the outer layer is the polyester composition (A) which has been described for the first hollow molded product, it should be
30 understood that the above description can be directly applied to the polyester composition forming the outer layer.

Further, it should be understood that the above description of the ultraviolet absorber for the above polyester composition (A) can be directly applied to the

ultraviolet absorber forming the inner layer.

The ultraviolet absorber contained in the outer layer and the ultraviolet absorber contained in the inner layer (when contained) of the first laminate hollow molded product
5 may be the same or different.

When the inner layer contains an ultraviolet absorber, the ultraviolet absorber contained in the inner layer is the same compound as the ultraviolet absorber contained in the outer layer and the content of the ultraviolet absorber in
10 the inner layer is preferably lower than that in the outer layer.

Further, the ethylene-2,6-naphthalene dicarboxylate polymer forming the inner layer and the ethylene-2,6-naphthalene dicarboxylate polymer forming the outer layer
15 may be the same or different in composition or molecular weight. It should be understood that the description of the first hollow molded product can be directly applied to the ethylene-2,6-naphthalene dicarboxylate polymer forming the inner layer.

20 The birefringence factor of the barrel portion consisting of the outer layer and the inner layer of the first laminate hollow molded product must be 0.17 or more.

The thickness of the barrel portion is preferably 0.15 to 0.8 mm, more preferably 0.20 to 0.60 mm. Further, the
25 thickness of the outer layer of the barrel portion is preferably 10 to 100 μm , more preferably 30 to 100 μm .

As for what is not described of the first laminate hollow molded product, it should be understood that the description of the first hollow molded product can be applied
30 directly or with modifications which are obvious for one of ordinary skill in the art.

According to the present invention, the first hollow molded product of the present invention is produced by the afore-mentioned first production process of the present

invention.

In the first production process, an ethylene-2,6-naphthalene dicarboxylate polymer and 0.01 to 5.0 wt%, based on the polymer, of an ultraviolet absorber are dry blended in the step (1). Alternatively, an ethylene-2,6-naphthalene dicarboxylate polymer and a master polymer which contains both the ethylene-2,6-naphthalene dicarboxylate polymer and an ultraviolet absorber in an amount of 1 to 10 wt% based on the above polymer may be prepared and dry blended to ensure that the desired content of the ultraviolet absorber should be 0.01 to 5.0 wt%.

Preferably, the above polymer to be dry blended has an intrinsic viscosity of 0.5 to 0.8. When the intrinsic viscosity is lower than 0.5, a reduction in the mechanical strength of the obtained hollow molded product becomes large. When the intrinsic viscosity is higher than 0.8, a reduction in intrinsic viscosity becomes large by shear heat generated due to high melt viscosity when a preform is molded in the subsequent step (2), and a by-product such as acetaldehyde formed by decomposition is contained in the hollow molded product in large quantities, thereby deteriorating flavor retention properties.

A generally used blender, for example, a V-type blender is advantageously used for dry blending.

The obtained dry blend is melt molded into a preform in the subsequent step (2).

Finally, the obtained preform is blow molded into a desired hollow molded product, that is, a hollow molded product whose barrel portion has a birefringence factor of 0.17 or more in the step (3).

The preform molding of the step (2) and the blow molding of the step (3) are known per se and known methods are employed.

A description is subsequently given of the second

hollow molded product, the third hollow molded product and the second production process of the present invention.

The second hollow molded product will be first described hereinunder.

5 The ethylene-2,6-naphthalene dicarboxylate polymer used in the second hollow molded product is the same polymer as the above ethylene-2,6-naphthalene dicarboxylate polymer used in the first hollow molded product.

 The polymer used in the second hollow molded product
10 is preferably obtained using an antimony compound or germanium compound as a polymerization catalyst.

 The glycol composition of polymer preferably contains cyclohexane dimethanol and/or neopentyl glycol in an amount of 20 mol% or less based on the total of all the glycol
15 components in addition to ethylene glycol.

 Preferably, the polymer has an aldehyde content of 30 ppm or less.

 The polyester composition (A) forming the second hollow molded product contains the above ethylene-2,6-naphthalene
20 dicarboxylate polymer and a pigment in an amount of 10 to 2,000 ppm.

 The pigment is at least one selected from the group consisting of an oxide pigment, ferrocyanide pigment, silicate pigment, phosphate pigment, carbon black,
25 condensation polycyclic pigment and phthalocyanine pigment. When the content of the pigment is lower than 10 ppm, the improvement of the color of the obtained hollow molded product and the absorption of radiation having a wavelength range special to the pigment become unsatisfactory. When the
30 content of the pigment is higher than 2,000 ppm, the transparency of the obtained hollow molded product lowers disadvantageously.

 The third hollow molded product of the present invention contains at least one pigment as described above.

This pigment serves to (1) improve the color of the hollow molded product, (2) protect contents from visible radiation, (3) shorten the molding cycle of the hollow molded product and make uniform the thickness of the hollow molded product.

5 As for the improvement of color, although the hollow molded product may be colored to enhance its product image, the production temperature and the molding temperature of the ethylene-2,6-naphthalene dicarboxylate polymer must be made higher than those of polyethylene terephthalate because
10 it has a high melting point and high melt viscosity and the polymer is readily colored by deterioration. The product value of the hollow molded product, for example, a container can be increased by containing a blue pigment, a purple pigment and a green pigment to make inconspicuous coloration
15 caused by deterioration at the time of production and molding.

 As for the protection of contents from visible radiation, since the ethylene-2,6-naphthalene dicarboxylate polymer can absorb an ultraviolet radiation range of 380 nm or less, it has no problem with protection from ultraviolet
20 radiation but there is a case where the contents of the hollow molded product must be protected from a visible radiation range of 500 nm or less. Therefore, the protection of the contents from visible radiation must be improved. A hollow molded product which can cut radiation having a desired
25 wavelength range and is colored without reducing its product value can be obtained by using a pigment or combining pigments to meet this requirement.

 As for a reduction in the molding cycle and uniformity in the thickness of the hollow molded product, an inorganic
30 compound and organic compound pigments are added to increase the absorption of an infrared radiation wavelength range with the result of an increase in the amount of heat received at the time of heating for the blow molding of the hollow molded product, thereby making it possible to shorten the molding

cycle. Further, since heat is easily and uniformly transmitted to every portion of the preform, nonuniform stretching is suppressed at the time of blow molding, thereby making it possible to make uniform the thickness of the hollow
5 molded product.

The oxide pigment is, for example, titanium dioxide, ferric oxide (red oxide), chromium oxide, cobalt blue (composite oxide pigment of cobalt oxide and aluminum oxide), zinc oxide (zinc white), lead tetroxide (red lead), cuprous
10 oxide (copper suboxide) or titanium nickel yellow. The ferrocyanide pigment is, for example, iron blue. The phosphate pigment is, for example, manganese violet. The condensation polycyclic pigment is, for example, an anthraquinone pigment. The phthalocyanine pigment is, for
15 example, Phthalocyanine Blue, non-metallic phthalocyanine, Phthalocyanine Green or Fast Sky Blue. The silicate pigment is preferably ultramarine blue, talc or white carbon. Preferred examples of the white carbon include silicic anhydride, hydrated silicic acid, hydrated magnesium
20 silicate, hydrated calcium silicate and hydrated aluminum silicate.

As for the second hollow molded product of the present invention, the haze of the barrel portion, which changes according to the content of the above pigment, must be 10 %
25 or less. When the haze is more than 10 %, transparency lowers, which is not preferred from the viewpoint of product value. The thickness of the barrel portion of the hollow molded product is preferably 150 to 800 μm , more preferably 200 to 600 μm .

30 Preferably, the second hollow molded product of the present invention has an acetaldehyde content in the ethylene-2,6-naphthalene dicarboxylate polymer of 30 ppm or less. When this content is higher than 30 ppm and the second hollow molded product is used as a food container for

containing specific contents, for example, water, it deteriorates in flavor retention properties that the flavor of the contents is impaired.

Methods of reducing the content of acetaldehyde to 30 ppm or less include one in which the ethylene-2,6-naphthalene dicarboxylate polymer as a raw material is solid-phase polymerized or crystallized at a temperature lower than its melting point, one in which the molding temperature for obtaining a preform by injection molding is reduced as much as possible, one in which a vented molding machine is used, and the like. Out of these methods, the method in which the polymer is solid-phase polymerized to fully reduce the content of acetaldehyde before melt molding is effective in reducing the content of acetaldehyde in the obtained hollow molded product. Therefore, the polymer used is preferably obtained by solid-phase polymerization.

The intrinsic viscosity of the polymer forming the second hollow molded product of the present invention is preferably 0.5 to 0.8. When the intrinsic viscosity is lower than 0.5, the strength of the hollow molded product lowers, or a molding failure such as thickness nonuniformity occurs at the time of blow molding. When the intrinsic viscosity is higher than 0.8, the melt viscosity becomes too high, resulting in poor moldability. As a result, the molding temperature is increased to improve moldability, whereby color deterioration caused by heat deterioration becomes marked disadvantageously.

The ethylene-2,6-naphthalene dicarboxylate polymer for forming the second hollow molded product of the present invention is preferably obtained by solid-phase polymerization after melt polycondensation because it can suppress color deterioration and reduce a by-product such as acetaldehyde. The solid-phase polymerization is preferably carried out at a temperature of 170° C or more and

the melting point or less for 3 to 30 hours, more preferably at 200°C or more and (melting point - 10)°C or less for 5 to 20 hours.

A description is subsequently given of the second
5 production process for producing the second hollow molded product of the present invention.

In the second production process, an ethylene-2,6-naphthalene dicarboxylate polymer and 10 to 2,000 ppm, based on the polymer, of a pigment are dry blended in the step (1).
10 Alternatively, an ethylene-2,6-naphthalene dicarboxylate polymer and a master polymer which contains both the above ethylene-2,6-naphthalene dicarboxylate polymer and a pigment in an amount of 0.01 to 1.0 wt% based on the above polymer may be prepared and dry blended to ensure that the
15 desired content of the pigment in the master polymer and the ethylene-2,6-naphthalene dicarboxylate polymer should be 10 to 2,000 ppm.

The latter process which uses the master polymer is preferred because the grade of the hollow molded product,
20 that is, the dry blending ratio can be easily changed when hollow molded products having different degrees of pigmentation are to be produced.

The concentration of the pigment contained in the master polymer is 0.01 to 1.0 wt%. When the concentration
25 of the pigment is lower than 0.01 wt%, the blending ratio of the master polymer becomes high so as to sufficiently color the obtained hollow molded product, which is economically disadvantageous. When the concentration of the pigment is higher than 1.0 wt%, the amount of the master polymer blended
30 becomes too small if the hollow molded product is colored a light color. As a result, it is difficult to make uniform the blending ratio and the obtained hollow molded product is apt to have nonuniformity in the degree of pigmentation.

In the present invention, preferred methods of

producing the master polymer containing a pigment in a high concentration include one in which the ethylene-2,6-naphthalene dicarboxylate polymer and the pigment are melt mixed together with an extruder, one in which the pigment
5 is added at any time from an ester exchange reaction or esterification reaction to the completion of a polycondensation reaction in the production of a polyester comprising an ethylene naphthalate unit as the main recurring unit, and the like.

10 When the master polymer is to be produced with an extruder, the extruder is not limited to a particular type and may be a single-screw or double-screw extruder, or vented or unvented extruder. The pigment is added in the form of powders or a slurry prepared by using a solvent which does
15 not substantially depolymerize the polymer, preferably a solvent which readily evaporates at a temperature higher than the melting point of the polymer, such as water or an organic solvent.

 When the pigment is added at any time from the ester
20 exchange reaction or esterification reaction to the completion of the polycondensation step, it is added in the form of a slurry prepared by using ethylene glycol, a volatile solvent which is not substantially copolymerized into the molecular chain of a polymer, or other copolymerizable glycol
25 component when the glycol components include the copolymerizable glycol component other than ethylene glycol.

 As for the dry blending ratio of the master polymer to the ethylene-2,6-naphthalene dicarboxylate polymer, the amount of the master polymer is preferably 0.5 to 10 wt% based
30 on the ethylene-2,6-naphthalate dicarboxylate polymer. When the amount of the master polymer is smaller than 0.5 wt%, the degree of pigmentation is small, a color improving effect is small, it is difficult to uniformly blend these, and there is a possibility that the degree of pigmentation

becomes nonuniform. When the amount of the master polymer is larger than 10 wt%, it is not preferred in terms of economy and quality. The reason why it is not preferred in terms of quality is that the content of acetaldehyde in a by-product produced when the master polymer is produced by melt mixing with an extruder increases and the master polymer is readily influenced by the difference in quality such as intrinsic viscosity between it and the ethylene-2,6-naphthalene dicarboxylate polymer to be blended.

10 In the second production process of the present invention, the dry blend obtained in the step (2) is melt molded into a preform.

Finally, the obtained preform is blow molded into a desired hollow molded product, that is, a hollow molded product having a haze of the barrel portion of 10 % or less in the step (3).

The preform molding of the step (2) and the blow molding of the step (3) are known per se and known methods are employed.

20 The third hollow molded product of the present invention is made from a polyester composition which comprises 0.01 to 5.0 wt% of a specific ultraviolet absorber which is the same as the ultraviolet absorber contained in the first hollow molded product and 10 to 2,000 ppm of a specific pigment which is the same as the pigment contained in the second hollow molded product. The barrel portion of the third hollow molded product has a birefringence factor (Δn) of 0.17 or more and a haze of 10 % or less.

The third hollow molded product has the above advantages of the first hollow molded product and the second hollow molded product.

30 It is easily understood by one of ordinary skill in the art that the third hollow molded product is produced in the same manner as the first hollow molded product and the second

hollow molded product.

All of the above hollow molded products may contain various additives such as a phenolic, organic sulfur-based or phosphite-based antioxidant, benzotriazole, triazine, 5 cyanoacrylate, benzooxazinone or benzophenone ultraviolet absorber, antistatic agent and the like as required.

The hollow molded product of the present invention can be used repeatedly. The step of washing with an alkali is included in the recycling cycle from filling to collection. 10 The preferred washing conditions include a temperature range of 50 to 95°C and an alkali concentration of 1 to 6 %. The washing time, which is changed by the washing temperature and the alkali concentration of a washing liquid, is preferably 5 to 60 minutes, more preferably 5 to 30 minutes.

15 The hollow molded product of the present invention is exposed to ultraviolet radiation such as sunlight during its repeated use. The illuminance of ultraviolet radiation during one-time of use is estimated at 7,500 to 90,000 mJ/cm² for a wavelength range of 310 to 400 nm.

20 The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting. The physical properties were measured in accordance with the following methods.

25 (1) refractive index

The center portion of the barrel portion of a bottle is cut out to measure the refractive index (nMD) in the axial direction of the bottle, the refractive index (nTD) in the 30 circumferential direction of the bottle and the refractive index (nZ) in the thickness direction of the bottle with the 4T Abbe's refractometer of Atago Co., Ltd. Nz is obtained by measuring refracted light passing through the interior surface when a sample is set in such a manner that the exterior

surface of the bottle is located at the top.

(2) haze

The barrel portion of a bottle is cut out and measured
5 with the turbidimeter of Nippon Denshoku Kogyosha Co., Ltd.

(3) color b value

A preform or bottle is crushed with a crusher,
crystallized at 170° C for 3 hours and measured for its color
10 b value with the Z-Σ80 of Nippon Denshoku Kogyosha Co., Ltd.

(4) concentration of carboxyl terminal groups

The mouth portion of a bottle is dissolved in benzyl
alcohol and titrated with a sodium hydroxide aqueous solution,
15 and the concentration of carboxyl terminal groups is obtained
from the equivalent of sodium hydroxide required for
titration. Phenol Red is used as an indicator and the time
when the color of the solution turns from yellow to light
orange is the end of titration.

20

(5) intrinsic viscosity

This is obtained from a solution viscosity measured at
35° C using a mixed solvent of phenol and tetrachloroethane
in a weight ratio of 6/4.

25

(6) content of acetaldehyde

A polymer is frozen and crushed to measure the content
of acetaldehyde with the HS-GC of Hitachi, Ltd.

30 (7) recycling test

A bottle is exposed to 30,000 mJ/cm² of ultraviolet
radiation using the XW-150 xenon tester of Shimadzu
Corporation each time. The illuminance of ultraviolet
radiation is measured with the UM-10 ultraviolet radiation

intensity meter of Minolta Co., Ltd. (UM-360 of light receiving portion).

The bottle is washed with an alkali at 85°C for 10 minutes. After the above treatment was repeated 15 times, the physical properties of the bottles of Examples and Comparative Examples were obtained.

Examples 1 to 9 and Comparative Examples 1 to 4

10 <production of polymer>

100 parts by weight of dimethyl 2,6-naphthalene dicarboxylate and 51 parts by weight of ethylene glycol were subjected to an ester exchange reaction in accordance with a commonly used method in the presence of 0.030 part by weight
15 of manganese acetate tetrahydrate (30 mmol% based on the dicarboxylic acid component) and 0.010 part by weight of cobalt acetate tetrahydrate (10 mmol% based on the dicarboxylic acid component). 20 minutes after methanol was distilled out, 0.012 part by weight of antimony trioxide (10
20 mmol% based on the dicarboxylic acid component) was added and 0.020 part by weight of phosphoric acid (1.25 times the number of moles of the ester exchange reaction catalyst) was added before the end of the ester exchange reaction.

Thereafter, a polycondensation reaction was carried out at
25 295°C and a high degree of vacuum to obtain an ethylene-2,6-naphthalene dicarboxylate prepolymer having an intrinsic viscosity of 0.50. The prepolymer was further solid-phase polymerized at 230°C for a residence time of 15 hours to obtain an ethylene-2,6-naphthalene dicarboxylate
30 polymer having an intrinsic viscosity of 0.65.

<production of master polymer containing ultraviolet absorber>

95 parts by weight of the ethylene-2,6-naphthalene

dicarboxylate polymer obtained in the production of the polymer above and 5 parts by weight of (3,1-benzooxazin-4-one) were melt mixed together with a double-screw extruder to obtain a master polymer which contains an
5 polyethylene-2,6-naphthalene dicarboxylate and an ultraviolet absorber.

<production of copolymer>

100 parts by weight of dimethyl 2,6-naphthalene
10 dicarboxylate, 48 parts by weight of ethylene glycol and 6 parts by weight of cyclohexane dimethanol or 4 parts by weight of neopentyl glycol were subjected to an ester exchange reaction in accordance with a commonly used method in the presence of 0.030 part by weight of manganese acetate
15 tetrahydrate (30 mmol% based on the dicarboxylic acid component) and 0.010 part by weight of cobalt acetate tetrahydrate (10 mmol% based on the dicarboxylic acid component). 20 minutes after methanol was distilled out, 0.012 part by weight of antimony trioxide (10 mmol% based
20 on the dicarboxylic acid component) was added, and 0.020 part by weight of phosphoric acid (1.25 times the number of moles of the ester exchange reaction catalyst) was added before the end of the ester exchange reaction. Thereafter, a
25 polycondensation reaction was carried out at 295° C and a high degree of vacuum to obtain an ethylene-2,6-naphthalene dicarboxylate prepolymer having an intrinsic viscosity of 0.50. This prepolymer was further solid-phase polymerized at 220° C for a residence time of 17 hours to obtain an
30 ethylene-2,6-naphthalene dicarboxylate polymer having an intrinsic viscosity of 0.70.

<molding of bottle>

A chip of the ethylene-2,6-naphthalene dicarboxylate polymer obtained in the production of the polymer above and

an ultraviolet absorber shown in Table 1 below were blended together in a predetermined ratio, the obtained blend was molded at 305°C using the 100MD injection molding machine of Meiki Seisakusho Co., Ltd. to obtain 55 g of a preform.

5 The obtained preform was blow molded into a bottle having an inner volume of 1.05 to 2.05 liters and a barrel portion thickness of 200 to 500 μm .

The center portion of the barrel portion of the obtained bottle was cut out and the refractive indices n_{MD} , n_{TD} and
10 n_{Z} in the axial, circumferential and thickness directions of the bottle were measured with an Abbe's refractometer to obtain Δn . Similarly, the barrel portion was cut out to measure its haze with a turbidimeter. These values are shown in Table 1 below.

15 The carboxyl terminal group concentration and the acetaldehyde content of the bottle were measured by cutting out a sample from the mouth portion of the bottle. The measurement of color-b value (Col-b) was carried out by crushing the preform of the bottle and crystallizing it at
20 170°C for 3 hours. The measurement values of physical properties are shown in Table 1 below.

Table 1

	polymer components			ultraviolet absorber component	amount based on polymer component (%)
	PEN component (mol%)	comonomer			
		component	quantity(mol%)		
Ex.1	100	-	-	a	0.7
Ex.2	100	-	-	a	0.7
Ex.3	100	-	-	a	1.0
Ex.4	100	-	-	b	0.5
Ex.5	100	-	-	c	0.2
Ex.6	100	-	-	d	6.0
Ex.7	90	A	10	a	0.5
Ex.8	90	B	10	a	0.5
Ex.9	100	-	-	e	1.0
C.Ex.1	100	-	-	-	-
C.Ex.2	100	-	-	a	6.0
C.Ex.3	100	-	-	b	0.5
C.Ex.4	90	A	10	a	0.5

Ex. = Example C.Ex. = Comparative Example

Table 1 (continued)

	physical properties of bottle						
	Δn	nZ	haze (%)	Col-b	COOH (eq/10 ⁶ g)	content of acetaldehyde (ppm)	
Ex. 1	0.210	1.523	6	1	19	15	
Ex. 2	0.225	1.501	4	1	19	15	
Ex. 3	0.215	1.516	2	2	20	14	
Ex. 4	0.221	1.514	13	3	20	20	
Ex. 5	0.208	1.521	12	1	18	18	
Ex. 6	0.205	1.527	10	2	24	25	
Ex. 7	0.198	1.533	3	2	27	26	
Ex. 8	0.190	1.535	3	2	25	26	
Ex. 9	0.219	1.509	4	3	20	15	
C.Ex. 1	0.209	1.517	30	1	14	16	
C.Ex. 2	0.215	1.520	10	15	20	20	
C.Ex. 3	0.160	1.551	21	3	20	20	
C.Ex. 4	0.155	1.555	26	2	25	26	

* The haze value is obtained after 15 times of repeated use.

Comonomers A and B and ultraviolet absorbers a to e in Table 1 are as follows (the same shall apply to Table 2).

comonomer A: cyclohexane dimethanol

comonomer B: neopentyl glycol

5 ultraviolet absorber a: (3,1-benzooxazin-4-one)

ultraviolet absorber b: 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol

ultraviolet absorber c: 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyloxy)phenol

10 ultraviolet absorber d: master polymer consisting of 95 parts by weight of a polyethylene naphthalate homopolymer and 5 parts by weight of (3,1-benzooxazin-4-one)

ultraviolet absorber e: (3,1-benzooxazin-4-one) + tetrakis(2,2,6,6-tetramethyl-4-piperidyl)1,2,3,4-butane

15 tetracarboxylate (1:1 mixture)

Examples 10 to 12 and Comparative Example 5

The polyethylene-2,6-naphthalene dicarboxylate (homopolymer) obtained in Examples 1 to 8 and an
20 ethylene-2,6-naphthalene dicarboxylate copolymer were used to mold a bottle having a weight of 32 g and an inner volume of 1.0 liter with the double-color molding machine of Nissei Jushi Co., Ltd.

The polymers of the outer layer and the inner layer used
25 for molding are shown in Table 2 and the physical properties of the obtained multi-layer bottle are shown in Table 3.

As obvious from the results of Examples 10 to 12, it can be said that ethylene-2,6-naphthalene dicarboxylate bottles containing an ultraviolet absorber and having high
30 An have the effect of suppressing an increase in haze during its repeated use and are of great product value.

Table 2

	outer layer				inner layer			
	polymer components		thickness	ultraviolet absorber		polymer component	component	amount based on polymer component (%)
	ethylene-2,6-naphthalene dicarboxylate (mol%)	comonomer quantity (mol%)	component	component	amount based on polymer component (%)			
Ex. 10	100	-	-	a	3.0	100	-	-
Ex. 11	100	-	50	b	1.0	100	-	-
Ex. 12	100	-	50	d	10	100	-	-
C. Ex. 5	90	A	50	-	-	100	-	-

Ex. = Example C.Ex. = Comparative Example

Table 3

	physical properties of bottle						
	Δn	nZ	haze (%)	Co1-b	COOH (eq/10 ⁶ g)	content of acetaldehyde (ppm)	
Ex.10	0.201	1.524	2	2	20	16	
Ex.11	0.199	1.532	2	1	21	15	
Ex.12	0.204	1.522	3	1	21	15	
C.Ex.5	0.188	1.542	31	2	26	18	

Ex. = Example C.Ex. = Comparative Example

Examples 13 to 18

(1) production of ethylene-2,6-naphthalene dicarboxylate polymer for bottles

100 parts by weight of dimethyl 2,6-naphthalene
5 dicarboxylate and 51 parts by weight of ethylene glycol were subjected to an ester exchange reaction in the presence of 0.030 part by weight of manganese acetate tetrahydrate (30 mmol% based on the acid component) and 0.010 part by weight of cobalt acetate tetrahydrate (10 mmol% based on the acid
10 component) by gradually elevating the temperature from 170° C. 20 minutes after methanol was distilled out, 0.012 part by weight of antimony trioxide (10 mmol% based on the acid component) was added and 0.020 part by weight of phosphoric acid (1.25 times the number of moles of the ester exchange
15 reaction catalyst) was added before the end of the ester exchange reaction. In Examples 16 and 17, germanium dioxide was used as a polycondensation catalyst and 0.015 part by weight of this germanium dioxide (35 mmol% based on the acid component) was added in place of antimony trioxide 10 minutes
20 before the end of the ester exchange reaction.

Thereafter, the reaction product was polycondensed at 295° C and a high degree of vacuum to obtain an ethylene-2,6-naphthalene dicarboxylate prepolymer having an intrinsic viscosity of 0.50. This prepolymer was further
25 solid-phase polymerized at 230° C for a residence time of 15 hours to obtain an ethylene-2,6-naphthalene dicarboxylate polymer for bottles having an intrinsic viscosity of 0.65.

(2) production of master polymer (1)

30 99.85 wt% of the ethylene-2,6-naphthalene dicarboxylate polymer for bottles obtained in (1) above and 0.15 wt% of Phthalocyanine Blue were melt mixed together with an extruder to obtain a blue master polymer (1).

(3) production of master polymer (2)

99.8 wt% of the ethylene-2,6-naphthalene dicarboxylate polymer for bottles obtained in (1) above and 0.2 wt% of a mixed pigment consisting of titanium nickel yellow / Phthalocyanine Green in a weight ratio of 1/4 were melt mixed together with an extruder to obtain a green master polymer (2).

(4) production of master polymer (3)

99 wt% of the ethylene-2,6-naphthalene dicarboxylate polymer for bottles obtained in (1) above and 1 wt% of a mixed pigment consisting of titanium nickel yellow / iron oxide red / carbon black in a weight ratio of 30/77/3 were melt mixed together with an extruder to obtain a brown master polymer (3).

(5) preparation of pigment

The following pigments were prepared.

pigment (1): mixed pigment of titanium nickel yellow and Phthalocyanine Green (weight ratio of 1/4)

pigment (2): Phthalocyanine Blue pigment

pigment (3): ultramarine blue pigment

(6) production of container

The ethylene-2,6-naphthalene dicarboxylate polymer for bottles obtained in (1) above, the master polymers (1) to (3) obtained in (2) to (4) above and the pigments (1) to (3) prepared in (5) above were blended in weight ratios shown in Table 4, and each of the obtained blends was molded into 55 g of a preform at 305°C using the 100DM injection molding machine of Meiki Seisakusho Co., Ltd. The obtained preform was blow molded into a bottle having an inner volume of 1.05 liters and a barrel portion thickness of 300 µm.

The physical properties of the obtained bottles are

shown in Table 4. They were excellent in transparency and color such that deterioration in the color of the ethylene-2,6-naphthalene dicarboxylate polymer was not conspicuous.

5

Examples 19 and 20

(1) production of ethylene-2,6-naphthalene dicarboxylate copolymer for bottles

92 parts by weight of dimethyl 2,6-naphthalene
10 dicarboxylate, 6.4 parts by weight of dimethyl terephthalate
and 51 parts by weight of ethylene glycol were subjected to
an ester exchange reaction in the presence of 0.030 part by
weight of manganese acetate tetrahydrate (30 mmol% based on
total of all the acid component) and 0.010 part by weight
15 of cobalt acetate tetrahydrate (10 mmol% based on total of
all the acid component) by gradually elevating the
temperature from 170°C. 20 minutes after methanol was
distilled out, 0.015 part by weight of germanium dioxide (35
mmol% based on total of all the acid components) was added
20 and 0.020 part by weight of phosphoric acid (1.25 times the
number of moles of the ester exchange reaction catalyst) was
added before the end of the ester exchange reaction.

Thereafter, the reaction product was polycondensed at
295°C and a high degree of vacuum of 1 mmHg or less to obtain
25 a ethylene-2,6-naphthalene dicarboxylate precopolymer
having an intrinsic viscosity of 0.56. The obtained
prepolymer was further solid-phase polymerized at 225°C for
18 hours to obtain an ethylene-2,6-naphthalene dicarboxylate
copolymer (PENT) for bottles having an intrinsic viscosity
30 of 0.76 and containing 8 mol% of terephthalic acid.

(2) production of container

The above ethylene-2,6-naphthalene dicarboxylate
copolymer (PENT) and the pigment (1) used in Examples 13 and

16 or the master polymer (1) were blended in a weight ratio shown in Table 4, and the obtained blend was molded into 55 g of a preform at 285°C using the 100 DM injection molding machine of Meiki Seisakusho Co., Ltd. The obtained preform
5 was blow molded into a bottle having an inner volume of 1.05 liters and a thickness of 300 µm.

The physical properties of the obtained ethylene-2,6-naphthalene dicarboxylate copolymer bottle container are shown in Table 4. It was excellent in transparency and
10 color.

Comparative Examples 6

A bottle was produced in the same manner as in Examples 13 and 16 except that the ethylene-2,6-naphthalene
15 dicarboxylate polymer for bottles used in Examples 13 and 16 and the pigment (1) or the mater polymer (1) used in Examples 13 and 16 were blended in a weight ratio shown in Table 4. The physical properties of the bottles are shown in Table 4.

20 When the concentration of the pigment is higher than that of the present invention, the obtained bottle is inferior in transparency which is not preferred from the viewpoint of product value. When the pigment or the pigment-containing master polymer is used in a small amount or not added, the
25 obtained bottle has no problem with transparency but is inferior in color with marked deterioration in the color of the polymer.

Comparative Examples 7 and 8

30 (1) production of ethylene-2,6-naphthalene dicarboxylate polymer for bottles

An ethylene-2,6-naphthalene dicarboxylate polymer for bottles was produced in the same manner as in Example 13 except that tetrabutyl titanate was used as a polycondensation

catalyst and added in place of antimony trioxide in an amount of 0.021 part by weight (15 mmol% based on the acid component) 10 minutes before the end of the ester exchange reaction.

5 (2) production of container

Bottles were produced in the same manner as in Example 13 except that the above ethylene-2,6-naphthalene dicarboxylate polymer for bottles and the pigment (1) used in Example 13 were blended in a weight ratio shown in Table 10 4. The physical properties of these bottles are shown in Table 4.

When a titanium compound was used, deterioration in the color of the polymer was more marked than when an antimony compound or germanium compound was used as a catalyst. When 15 a small amount of the pigment was added, this improving effect was small and a bottle which was inferior in product value was obtained.

Reference Example 1

20 A bottle was obtained in the same manner as in Example 19 except that the pigment or the pigment-containing master polymer was not added. The physical properties of this bottle are shown in Table 4.

Table 4

	polymer		type of catalyst (quantity) (mmol%)	pigment	
	composition	IV		type	quantity (ppm)
Ex. 13	PEN(100)	0.65	Sb(10)	pigment (1)	500
Ex. 14	PEN(100)	0.65	Sb(10)	pigment (2)	50
Ex. 15	PEN(100)	0.65	Sb(10)	pigment (3)	1500
Ex. 16	PEN(100)	0.65	Sb(10)	-	-
Ex. 17	PEN(100)	0.65	Ge(35)	-	-
Ex. 18	PEN(100)	0.65	Ge(35)	-	-
Ex. 19	PENT(100)	0.76	Ge(35)	pigment (1)	400
Ex. 20	PENT(100)	0.76	Ge(35)	-	-
C.Ex. 6	PEN(100)	0.65	Sb(10)	pigment (1)	3000
C.Ex. 7	PEN(100)	0.65	Ti(15)	-	-
C.Ex. 8	PEN(100)	0.65	Ti(15)	pigment (1)	5
Ref.Ex. 1	PENT(100)	0.76	Ge(35)	-	-

Ex. = Example C.Ex. = Comparative Example Ref.Ex. = Referential Example

Table 4 (continued)

	master polymer		blending ratio (weight ratio) MB/polymer	physical properties of bottle		
	type			Col-b	haze (%)	AA (ppm)
Ex.13	-		-	-2	1.1	18
Ex.14	-		-	-16	1.5	18
Ex.15	-		-	-15	6.3	17
Ex.16		master polymer (1)	1/30	-15	1.4	20
Ex.17		master polymer (2)	1/50	0	1.0	24
Ex.18		master polymer (3)	1/30	0	7.2	23
Ex.19	-		-	-1	1.0	15
Ex.20		master polymer (1)	1/40	-12	1.2	17
C.Ex.6	-		-	15	13	19
C.Ex.7	-		-	10	1.2	26
C.Ex.8	-		-	8	1.1	30
Ref.Ex.1	-		-	1	1.0	20

MB: master polymer

PEN: polyethylene-2,6-naphthalene dicarboxylate

5 PENT: ethylene-2,6-naphthalene dicarboxylate copolymer comprising 8 mol% of terephthalic acid

AA: content of acetaldehyde (ppm)

pigment (1): mixed pigment of titanium nickel yellow / Phthalocyanine Green (weight ratio of 1/4)

pigment (2): Phthalocyanine Blue

pigment (3): ultramarine blue

CLAIMS

1. A hollow molded product (A1) which comprises a polyester composition comprising an ethylene-2,6-naphthalene dicarboxylate polymer which has 2,6-naphthalenedicarboxylic acid component in an amount of at least 80 mol% based on the total of all the dicarboxylic acid components and ethylene glycol component in an amount of at least 80 mol% based on the total of all the glycol components and at least one ultraviolet absorber selected from the group consisting of a benzotriazole compound, triazine compound, benzophenone compound, cyanoacrylate compound and benzooxazinone compound in an amount of 0.01 to 5.0 wt% based on the ethylene-2,6-naphthalene dicarboxylate polymer, and (B1) which has a birefringence factor (Δn) of the barrel portion of 0.17 or more.
2. The hollow molded product of claim 1, wherein the barrel portion has a haze of 15 % or less.
3. The hollow molded product of claim 1, wherein the barrel portion has a refractive index (n_z) in a thickness direction of 1.54 or less.
4. The hollow molded product of claim 1 which has a b-value of 5 or less.
5. The hollow molded product of claim 1, wherein the ethylene-2,6-naphthalene dicarboxylate polymer has a carboxyl terminal group concentration of 32 equivalents / 10^6 g of the polymer or less.
6. The hollow molded product of claim 1, wherein the ethylene-2,6-naphthalene dicarboxylate polymer has an

aldehyde content of 30 ppm or less.

7. The hollow molded product of claim 1, wherein the ethylene-2,6-naphthalene dicarboxylate polymer has at least one glycol component selected from the group consisting of cyclohexane dimethanol and neopentyl glycol in an amount of 20 mol% or less based on the total of all the glycol components.

8. The hollow molded product of claim 1, wherein the polyester composition further comprises an hindered amine antioxidant in an amount of 0.1 to 5.0 wt% based on the ethylene-2,6-naphthalene dicarboxylate polymer.

9. The hollow molded product of claim 1 which is a bottle.

10. A preform for producing the hollow molded product of claim 1.

11. A hollow molded product which has a laminate structure consisting of an outer layer of the polyester composition of claim 1 and an inner layer of an ethylene-2,6-naphthalene dicarboxylate polymer which does not contain an ultraviolet absorber or contains at least one ultraviolet absorber selected from the group consisting of the ultraviolet absorbers specified in claim 1 and has a birefringence factor of the barrel portion of 0.17 or more.

12. The hollow molded product of claim 11, wherein the inner layer contains an ultraviolet absorber which is the same compound as the ultraviolet absorber contained in the outer layer and the content of the ultraviolet absorber in the inner layer is lower than the content of the ultraviolet absorber in the outer layer.

13. The hollow molded product of claim 11, wherein the outer layer has a thickness of 10 to 100 μm .
- 5 14. The hollow molded product of claim 11 which is a bottle.
15. A preform for producing the hollow molded product of claim 11.
- 10 16. A process for producing a hollow molded product comprising the steps of:
- (1) dry blending an ethylene-2,6-naphthalene dicarboxylate polymer which comprises 2,6-naphthalenedicarboxylic acid component in an amount of at least 80 mol% based on the total of all the dicarboxylic acid components and ethylene glycol component in an amount of at least 80 mol% based on the total of all the glycol components with at least one ultraviolet absorber selected from the group consisting of a benzotriazole compound, triazine compound, 20 benzophenone compound, cyanoacrylate compound and benzooxazinone compound in an amount of 0.01 to 5.0 wt% based on the ethylene-2,6-naphthalene dicarboxylate polymer, or dry blending the above ethylene-2,6-naphthalene dicarboxylate polymer with a master polymer which contains 25 both the above ethylene-2,6-naphthalene dicarboxylate polymer and at least one of the above ultraviolet absorbers in an amount of 1 to 10 wt% based on the ethylene-2,6-naphthalene dicarboxylate polymer to ensure that the content of the ultraviolet absorber should become 0.01 to 5.0 wt% 30 based on the ethylene-2,6-naphthalene dicarboxylate polymer;
- (2) melt molding the obtained dry blend into a preform; and
- (3) blow molding the obtained preform into the hollow molded product having a birefringence factor of the barrel

portion of 0.17 or more.

17. A hollow molded product (A2) which comprises a polyester composition comprising an ethylene-2,6-
5 naphthalene dicarboxylate polymer which has 2,6-naphthalenedicarboxylic acid component in an amount of at least 80 mol% based on the total of all the dicarboxylic acid components and ethylene glycol component in an amount of at least 80 mol% based on the total of all the glycol components
10 and at least one pigment selected from the group consisting of an oxide pigment, ferrocyanide pigment, silicate pigment, phosphate pigment, carbon black, condensation polycyclic pigment and phthalocyanine pigment in an amount of 10 to 2,000 ppm, and (B2) which has a haze of the barrel portion of 10 %
15 or less.

18. The hollow molded product of claim 17, wherein a polymerization catalyst for the ethylene-2,6-naphthalene dicarboxylate polymer is an antimony compound or a germanium
20 compound.

19. The hollow molded product of claim 17, wherein the ethylene-2,6-naphthalene dicarboxylate polymer has an acetaldehyde content of 30 ppm or less.
25

20. The hollow molded product of claim 17, wherein the ethylene-2,6-naphthalene dicarboxylate polymer has at least one glycol component selected from the group consisting of cyclohexane dimethanol and neopentyl glycol in an amount of
30 20 mol% or less based on the total of all the glycol components.

21. The hollow molded product of claim 17 which is a bottle.

22. A preform for producing the hollow molded product of claim 17.

23. A process for producing a hollow molded product
5 comprising the steps of:

(1) dry blending an ethylene-2,6-naphthalene
dicarboxylate polymer which comprises 2,6-
naphthalenedicarboxylic acid component in an amount of at
least 80 mol% based on the total of all the dicarboxylic acid
10 components and ethylene glycol component in an amount of at
least 80 mol% based on the total of all the glycol components
with at least one pigment selected from the group consisting
of an oxide pigment, ferrocyanide pigment, silicate pigment,
phosphate pigment, carbon black, condensation polycyclic
15 pigment and phthalocyanine pigment in an amount of 10 to 2,000
ppm, or dry blending the above ethylene-2,6-naphthalene
dicarboxylate polymer with a master polymer which contains
both the above ethylene-2,6-naphthalene dicarboxylate
polymer and at least one of the above pigments in an amount
20 of 0.01 to 1.0 wt% based on the ethylene-2,6-naphthalene
dicarboxylate polymer to ensure that the content of the
pigment should become 10 to 2,000 ppm;

(2) melt molding the obtained dry blend into a preform; and

(3) blow molding the obtained preform into the hollow
25 molded product having a haze of the barrel portion of 10 %
or less.

24. The process of claim 23, wherein the master polymer has
been prepared by melt mixing the ethylene-2,6-naphthalene
30 dicarboxylate polymer and the pigment with an extruder.

25. The process of claim 23, wherein the master polymer has
been produced by adding a pigment at any point from an ester
exchange reaction to the end of a polycondensation reaction

for the production of the ethylene-2,6-naphthalene dicarboxylate polymer or any point from a direct esterification reaction to the end of the polycondensation reaction.

5

26. The process of claim 23, wherein the master polymer is used in an amount of 0.5 to 10 wt% based on the ethylene-2,6-naphthalene dicarboxylate polymer.

10 27. A hollow molded product (A3) which comprises a polyester composition comprising an ethylene-2,6-naphthalene dicarboxylate polymer which has 2,6-naphthalenedicarboxylic acid component in an amount of at least 80 mol% based on the total of all the dicarboxylic acid
15 components and ethylene glycol component in an amount of at least 80 mol% based on the total of all the glycol components, at least one ultraviolet absorber selected from the group consisting of a benzotriazole compound, triazine compound, benzophenone compound, cyanoacrylate compound and
20 benzooxazinone compound in an amount of 0.01 to 5.0 wt% based on the ethylene-2,6-naphthalene dicarboxylate polymer, and at least one pigment selected from the group consisting of an oxide pigment, ferrocyanide pigment, silicate pigment, phosphate pigment, carbon black, condensation polycyclic
25 pigment and phthalocyanine pigment in an amount of 10 to 2,000 ppm, (B3) which has a birefringence factor (Δn) of the barrel portion of 0.17 or more and (B4) which has a haze of the barrel portion of 10 % or less.