

BILAYER CONTAINER

The present invention relates to a liquid bleach disposed in a bilayer container and stably stored.

An aqueous solution of a hypochlorite or hydrogen peroxide has been widely used heretofore for bleaching clothes, removing dirt from hard surfaces of tableware and articles in a toilet room or a lavatory and removing moulds, because it is a liquid which is convenient to use.

Such liquid bleach is usually in the form of a 0.5 to 10 weight % aqueous solution disposed in a resin bottle made of a flexible plastic material with a high tightness, such as polyethylene, and is readily available on the market as a household liquid bleach. In addition, liquid bleaches are available on the market in the form of an aqueous solution of other inorganic peroxy acids or organic peroxy acids or dispersions thereof in a solvent.

Liquid bleaches sometimes decompose depending on the storage conditions giving off an unpleasant odour or causing deformation of the bottle when gas is given off in large amounts. In view of these problems investigations have been made on the composition of the liquid bleaches for the purpose of improving storability. For example, in order to improve the storability of an aqueous hypochlorite solution, U.S.P. No.4029591

discloses that the addition of a specified polyoxyethylene alkylphenol sulfate is effective and Japanese Patent Laid-Open No.89800/1987 discloses that the addition of a specified perfume component is effective.

Further investigations have been made in an attempt to improve the storability of an aqueous hydrogen peroxide solution. Japanese Patent Publication No.775/1965 discloses a weakly acidic liquid bleach comprising acid sodium pyrophosphate, neutral sodium pyrophosphate and neutral potassium pyrophosphate having a high storability; U.S.P. No.3811833 and G.B.P. No.1419184 disclose a stable liquid bleach comprising an organic acid selected from among alkylidenediphosphonic acids, ethylenediamine-tetraacetic acid, diethylenetriaminepentaacetic acid and nitrilotrimethylenephosphonic acid, a soluble tin salt and an ammonium salt and having a pH of 0.5 to 7; U.S.P. No.4363699 and G.B.P. No.1524013 disclose a stabilizer for hydrogen peroxide which comprises poly- α -hydroxyacrylic acid; Japanese Patent Laid-Open No.10309/1979 discloses that the decomposition of hydrogen peroxide is inhibited at a pH of 4 to 6 with a hydrophilic liquid substance obtained by adding water to a magnesium compound and an acid to form a complex by neutralization; U.S.P. No.4238192 and E.P. No.13886 disclose a stable liquid bleach having a pH of 1.8 to 5.5

which comprises an acid selected from organic acids, phosphoric acid and boric acid and a nitrogen compound; Japanese Patent Laid-Open No.76161/1980 discloses that a synergistic stabilization effect can be obtained by incorporating a poly- α -hydroxyacrylic acid salt into an alkaline hydrogen peroxide bleach containing a polyphosphate as the stabilizer; Japanese Patent Laid-Open No.154457/1982 discloses a stabilizing assistant for a hydrogen peroxide bleach which comprises a copolymer of acrylic acid with an acrylate and/or polyethylene glycol methacrylate; and Japanese Patent Laid-Open No. 185797/1987 discloses a stabilizer for hydrogen peroxide bleach which comprises a poly- α -hydroxyacrylic acid salt and an organic phosphonic acid salt.

However, the liquid bleaches are also unstable to light and therefore, a liquid bleach composition having a high stability on its own is insufficient for selling as a commercial product. Thus liquid bleach compositions are placed on the market in highly light-screening, thick-walled, coloured resin bottles.

Although no problem arises when liquid bleach products are kept in a store or a dark, cold place, it has been found recently that a pigment usually incorporated into the resin from which the bottle is made for the purposes of screening light and improving the appearance of the bottle to appeal to the consumer accelerates the decomposition of the contents of the

bottle, i.e. a liquid bleach by giving off a gas when the bottle is exposed to high-temperatures for a long period of time.

However, the interaction between the pigment incorporated into the resin of the bottle and the liquid bleach contained in the bottle has never been discussed heretofore and no improvement for inhibiting gas production has been attempted.

A multilayer container has been used for food and drink and occasionally for the purpose of preventing contamination of the food and drink by the inorganic filler incorporated into the resin of the container. For example, Japanese Patent Laid-Open No.253539/1985 discloses a multilayer container which comprises an outer layer made of a resin composition composed of 20 to 80% by weight of inorganic filler(s) and 80 to 20% by weight of thermoplastic resin(s) and a inner layer made of a resin composition composed of a polyethylene and a polypropylene and no inorganic filler.

An object of the present invention is to provide a liquid bleach disposed or filled in a container or vessel capable of effectively inhibiting decomposition of the liquid bleach, even under severe conditions.

After intensive investigations it has been found that the object of the present invention can be attained

by using a thermoformed container made of a specified resin laminate.

The present invention provides a liquid bleach disposed or filled in a bilayer container comprising a liquid bleach composition and a bilayer container, the bilayer container having an outer layer (A) comprising a polyolefin and a pigment and a pigment-free inner layer (B) of polyolefin, wherein the ratio of thickness of layer (A) to layer (B) is 99:1 to 55:45.

It is preferable that the layer (A) comprises 99 to 80% by weight of the thermoplastic resin(s) and 1 to 20% by weight of the pigment(s).

Furthermore, it is preferable that the pigment is selected from the group consisting of a pigment of phthalocyanine group, that of azo group, that of metal oxide, carbon black and a mixture thereof.

The thermoplastic resin used is preferably a polyethylene, more preferably a low-density polyethylene.

The liquid bleach composition is preferably an aqueous hydrogen peroxide solution.

Furthermore, the present invention provides a bilayer container for housing a liquid bleach composition having an outer layer (A) comprising a polyolefin resin and a pigment and a pigment-free inner layer (B) comprising a polyolefin, wherein the ratio of thickness of the layer (A) to that of layer (B) is 99:1 to 55:45.

The present invention will become more fully understood from the detailed description given hereinbelow and the accompanying drawing which is given by way of illustration only.

Fig. 1 is a partially broken front view of the bilayer container of the present invention.

The polyolefins used for forming layer (A) are not particularly limited and include those which can be molded under ordinary conditions of thermoforming bottles. Examples of polyolefins include polyethylenes (eg. high-density polyethylene, low-density polyethylene and linear low-density polyethylene) and polypropylene (eg. homopolymers, block copolymers and random copolymers).

When a polyolefin resin is used, polyethylene, polypropylene and polybutene resins can be used either alone or in the form of a mixture. When the bilayer containers of the present invention are to be continuously produced on a large scale by a thermoforming method such as blow molding, it is advantageous to use resins of the same family.

The polyolefins used for forming layer (B) are not particularly limited and those described above for layer (A) can be used. Although the thermoplastic resin of layer (A) may be different from that of layer (B), they are preferably made of the same one.

Various pigments can be used in layer (A). Organic pigments usable therein include azo, anthraquinone, phthalocyanine, perinone, perylene, quinacridone, dioxazine, thioindigo and isoindolinone pigments and mixtures thereof. Inorganic pigments usable therein include metal oxides such as red iron oxide, titanium white, titanium yellow, fired pigment green, chromium oxide, cobalt blue, silica and

alumina; sulfides such as cadmium yellow and cadmium red; silicates such as ultramarine; chromates such as chrome yellow and chromium vermillion; carbons such as carbon black; clays such as talc, kaolin and clay; inorganic salts such as calcium carbonate, magnesium carbonate, calcium sulfite, calcium sulfate, aluminum hydroxide, barium sulfate and magnesium carbonate; and mixtures thereof. In particular, phthalocyanine, azo and metal oxide pigments and mixtures thereof have excellent weather resistance, light-screening properties, thermal resistance, color-developing properties and chemical resistance, so that they are preferably used.

When a phthalocyanine or azo pigment is used, the variety or form thereof is not particularly limited. For example, highly purified pigments or those heat-treated to remove impurities therefrom can be used and, in addition, those containing a small amount of impurities can also be used.

When titanium white among the metal oxides is used in combination with the organic pigment, the titanium white usually refers to titanium dioxide (TiO_2), which may be one containing a small amount of titanium monoxide (TiO) or dititanium trioxide (Ti_2O_3) as well as a small amount of impurities such as

silica, alumina, heavy metals and metal oxides, which pose no problem at all. The form of the titanium oxide is not particularly limited.

A material for layer (A) in the present invention is prepared by kneading 99.99 to 50% by weight, preferably 99 to 80% by weight, of the polyolefin and 0.01 to 50% by weight, preferably 1 to 20% by weight, of the pigment. If necessary, various antioxidants, ultraviolet absorbers, antistatic agents and lubricants can be added to the material for layer (A).

A material for layer (B) in the present invention is a chip or a sheet made of the polyolefin, for example. If necessary, various antioxidants, ultraviolet absorbers, antistatic agents and lubricants can be added to the material of layer (B).

The bilayer container or vessel used in the present invention has the pigmented olefin layer (A) and the pigment-free olefin layer (B), and layer (B) is disposed inside layer (A). Namely, layer (B) is served as the inner layer.

Fig. 1 shows one example of the two-layered

container of the present invention having layer (B) disposed inside layer (A).

The thickness ratio of layer (A) to layer (B) is not particularly limited. It is suitably determined depending on the variety and amount of the thermoplastic resin(s) and pigment(s) used. As for the layer thickness ratio of a two-layered container, that of layer (A) to layer (B) is 99 : 1 to

55 : 45, the thickness of the total layers being 100. The average wall thickness of the multilayer container is usually about 0.5 to 1.5 mm.

The container used in the present invention can be produced by various methods which are not particularly limited. For example, a laminated sheet comprising layers (A) and (B) can be thermoformed into an intended container by blow molding and the like.

The liquid bleach composition used in the present invention includes those comprising an ordinary aqueous solution of a hypochlorite or hydrogen peroxide as the bleaching base and other ordinary components. The composition is also not particularly limited.

The following Examples will further illustrate

the present invention, which by no means are intended to limit the scope of the present invention.

(Example 1)

Bottles made of a resin and a resin composition and having a layer thickness ratio as specified in Table 2 were formed to give a multilayer container for liquid bleach having the shape shown in Fig.1. Each of the bottles thus obtained was filled with a liquid bleach composition specified in Table 1 and tightly sealed. The bottles were examined by the following test method.

(Test Method)

100 ml of a liquid bleach composition shown in Table 1 was poured into each bottle (capacity: 1150 ml, average wall thickness: 1 mm) listed in Table 2 and the bottle was tightly closed and stored under the following conditions:

- (1) 50°C for 30 days, or
- (2) exposure to solar rays for 30 days (the maximum temperature: 30°C, the minimum temperature: 22°C).

After storage tests, the samples were taken out and those subjected to the test condition (1) were examined with the naked eye for any bulging or deformation of the bottles, while those subjected to the test condition (2) were examined for a change in the smell of the liquid bleach compositions in the bottles.

The criteria for measuring the bulge of the bottles

and change in the smell of the liquid bleach compositions were given below. 10 bottles were used in each test and the results were given in terms of the number of samples evaluated to be o, Δ or x.

Criteria of evaluation:

(1) Bulge of the bottle:

o: no change

Δ: the bottom of the bottle slightly bulged but
the bottle stood stable.

x the bottom of the bottle slightly bugled and the
bottle could not stand stable.

(2) Change in smell:

o: none

Δ: slight

x: discernible

Table 1 Bleach composition

Hydrogen peroxide	5
Sodium linear alkylbenzene-sulfonate ^{*1)}	0.5
Polyoxyethylene alkyl ether ^{*2)}	2
Dequest 2010 ^{*3)}	0.1
NaOH	in a minute amount ^{*4)}
Fragrance or Perfume	0.05
Deionized water	the balance
pH	4

(unit: wt. %)

- *1) alkyl: C₁₂
- *2) alkyl: C₁₂ to C₁₄, ethylene oxide (8 mol) adduct
- *3) 1-hydroxyethylidene-1,1-diphosphonic acid mfd. by Mitsubishi Monsanto Chemical Co.
- *4) an amount necessary for adjusting the pH to 4.

Table 2

			Comparative		Present invention						
			1	2	3	4	5	6	7		
Resin compo- sition	Layer (B)	LDPE*1)	100 parts by wt.		100	100	100	100	100	100	
	Layer (A)	LDPE*1)		95 parts by wt.	95	95	95	80	99		
		titanium white		5 parts by wt.	5	5	4.5	18	1		
		cyanine green				0.25					
Layer ratio*2) [layer (A)/layer (B)]			0.00/1.00	1.00/0.00	0.55/0.45	0.90/0.10	0.80/0.20	0.44/0.36	1.26/0.09		
Results	(1) stored at 50°C for 30 days	o	10	0	10	10	10	10	10		
		Δ	0	5	0	0	0	0	0		
		x	0	5	0	0	0	0	0		
	(2) exposed to solar rays	o	0	10	10	10	10	10	10		
		Δ	2	0	0	0	0	0	0		
		x	8	0	0	0	0	0	0		

#1) low-density polyethylene resin: Sholex 5503D mfd. by Showa Denko K.K.

#2) The average wall thickness of the container as well as the thickness of the layer (A) and that of the layer (B) are expressed in mm.



CLAIMS

1. A bilayer container for storing a liquid bleach composition comprising hydrogen peroxide, the container having outer layer (A) comprising polyolefin and pigment and a pigment-free inner layer (B) of polyolefin, wherein the ratio of thickness of the layer (A) to that of the layer (B) is 99 : 1 to 55 : 45.

2. A bilayer container as claimed in Claim 1, wherein the layer (A) comprises 99 to 80% by weight of the polyolefin resin(s) and 1-20% by weight of the pigment(s).

3. A bilayer container as claimed in any one of Claims 1 or 2, wherein the pigment is selected from the group consisting of a pigment of phthalocyanine group, a pigment of azo group, a pigment of metal oxide, carbon black, or a mixture thereof.

4. A bilayer container as claimed in any one of Claims 1 to 3, wherein the polyolefin is polyethylene.

5. A bilayer container as claimed in Claim 4, wherein the polyethylene is a low-density polyethylene.

6. A liquid bleach disposed in a bilayer container comprising a liquid bleach _____ and a thermoformed bilayer container, the thermoformed bilayer container having a outer layer (A) comprising polyolefin and pigment and a pigment-free inner layer (B) of polyolefin, wherein the ratio of thickness of the layer (A) to that of the layer (B) is 99 : 1 to 55 : 45.



7. The liquid bleach disposed in a bilayer container according to Claim 6, wherein the layer (A) comprises 99 to 80% by weight of polyolefin and 1 to 20% by weight of the pigment(s).

8. The liquid bleach disposed in a bilayer container according to Claim 7, wherein the pigment is selected from the group consisting of a pigment of phthalocyanine group, a pigment of azo group, a pigment of metal oxide, carbon black and a mixture thereof.

9. The liquid bleach disposed in a bilayer container according to Claim 8, wherein the polyolefin is a polyethylene.

10. The liquid bleach disposed in a bilayer container according to Claim 9, wherein the polyethylene is a low-density polyethylene.