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54 **Materials containing hinokitiol for preserving freshness of edible materials and method of preserving freshness of same.**

57 **A packaging film comprising at least one compound selected from the group consisting of hinokitiol and salts thereof and cyclodextrin inclusion compounds containing the same, and optionally, at least one barrier layer laminated on the outer surface of the synthetic resin film.**

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## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

5 The present invention relates to a material for preserving the freshness of edible materials such as vegetables and fruits as well as a method of preserving the freshness of same. More specifically, it relates to a synthetic resin film comprising, for example, hinokitiol and a wrapping film comprising a synthetic resin film composed of, for example, hinokitiol, and a barriers layer, as well as a material for and a method of preserving the freshness of edible materials such as vegetables and fruits in which the above-mentioned  
 10 synthetic resin film is employed.

The term "vegetables and fruit" as used herein means greens, vegetables and fruit after harvesting; and greens, vegetables and fruit such as rootcrops, beans, potatos, sweet potatos, and cereals which are processed through peeling or busking; vegetables and fruit which are processed by slicing or cutting into fine pieces, such as cut vegetables; or vegetables and fruit lightly processed by a light drying or  
 15 dehydration operation.

## 2. Description of the Related Art

Many types of greens, vegetables and fruit continue to ripen even after harvesting, and a variety of  
 20 changes thus occur, such as in the scent and color and a softening of the pulp. Nevertheless, there greens, vegetables and fruit, depending on the kind thereof, are still edible even if harvested before ripening, i.e., when still not ripe, as long as they are matured to a certain extent by a containing ripening process after harvesting.

This ripening of the greens, vegetables and fruit after harvesting is called "post ripening", and the  
 25 transportation and storage thereof is sometimes based on the use of this phenomenon, i.e., in general, this post ripening phenomenon is inhibited or accelerated to achieve a desired purpose. As a means for extending the transportation or storage time through the inhibition of the post ripening phenomenon of the greens, vegetables and fruit, there is conventionally known a method which comprises absorbing ethylene, which becomes a cause of an increase in the respiration action of greens, vegetables and fruits,  
 30 accompanied by the post ripening thereof (i.e., climacteric rise) (see Japanese Unexamined Patent Publication (Kokai) No. 56-88752).

In addition, as a means of preventing a putrefaction of greens, vegetables and fruit due to a proliferation of microorganisms (such as mold) a variety of methods have been proposed. For examples, method in which the edible materials to be wrapped are washed with an aqueous solution of sodium chloride or  
 35 chlorine water; a method in which greens, vegetables and fruit are stored in a corrugated fiberboard container or a bag of a synthetic resin together with an alcohol preparation or a substance such as a synthetic resin film or a nonwoven fabric having a surface coated with an antibiotic substance; or a method in which a fungicide is directly sprayed over greens, vegetables and fruit, in the form of a mist.

Regarding the other edible materials such as processed fish products, raw, processed or cooked  
 40 chickens, porks and beefs, as a means of preventing a putrefaction of the edible materials due to a proliferation of microorganisms such as mold or bacteria, various methods have been proposed. For examples, vacuum wrapping and gas replacement wrapping techniques are known in the art. Various techniques by which the proliferation of microorganisms in the edible materials is prevented or suppressed by eliminating oxygen from the atmosphere of the wrapped edible materials have been studied and  
 45 practiced. Further, the edible materials to be wrapped are washed with an aqueous sodium chloride solution or chlorine water, or antimold agents are used. In processed foods, food preservatives, alcoholic preparations, deoxidants or the like are added. Furthermore, it has been proposed that antibiotic substances be coated on the surfaces of wrapping synthetic resin films or nonwoven fabrics or germicides be directly sprayed in the form of a mist over the edible materials.

50 These proposals, however, still have the following disadvantages. Namely, since additional washing steps are used or since preservatives are directly incorporated into the edible materials, the qualities, such as taste, are liable to deteriorate. When the alcoholic preparations, deoxidants or the like are used, additional cumbersome work is needed to fill the alcoholic preparations or deoxidants or the like into the wrapping bags, or there is some danger that such additives may be erroneously eaten. Furthermore, when  
 55 the antibiotics are coated on the surfaces of the wrapping materials, the effects largely depend upon the conditions or environments under which the wrapping is carried out, the loss of the antibiotics is large, and a sustained release thereof cannot be arbitrarily controlled.

Furthermore, a method has been proposed which comprises adsorbing a substance which is safe and

can inhibit the proliferation of microorganisms on an appropriate article, such as a variety of packaging materials or adhesive materials, and then bringing it into contact with the surface of the edible materials, or packaging edible materials with such a packaging material, and it has been disclosed that excellent results can be obtained if hinokitiol, a salt thereof, or an inclusion compound containing the same is used as the above-mentioned substance (see, for example, Japanese Unexamined Patent Publication (Kokai) No. 61-108359).

As stated above, the adsorption of ethylene or water and the prevention of decay have been conventionally investigated for the preservation of the freshness of edible materials, but the above-mentioned conventional techniques require cumbersome operations such as a washing process after, for example, harvesting the greens, vegetables and fruit and operations for introducing same into a corrugated fiberboard container or a bag of a synthetic resin together with, for example, an alcoholic preparation. Moreover, a large amount of antibiotic substances is lost when the surface-coated materials are employed, the sustained release properties thereof cannot be arbitrarily controlled, and this method suffers from various problems, depending on the washing process and the kind of preparations used, in that the quality of the edible materials becomes poor, and that the method provides an insufficient safety. Therefore, it is difficult to properly preserve the freshness of the edible materials during, for example, the storage and transportation thereof.

## SUMMARY OF THE INVENTION

Accordingly, the objects of the present invention are to eliminate the above-mentioned disadvantages of the prior art and to develop a packaging material by which it becomes possible to sufficiently inhibit the post ripening phenomenon of greens, vegetables and fruit through a suppressing of any increase in the respiration action thereof; to substantially extend the storage time of the edible material through a drastic improvement in the effect of inhibiting the proliferation of microorganisms, to minimize the number of pretreatments, to eliminate cumbersome operations such as packaging and to improve the commercial value of the edible materials, to develop a synthetic resin film to be used as a material for making the packaging material, and a method of preserving the edible materials using same.

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

In accordance with the present invention, there is provided a synthetic resin film which comprises at least one compound selected from the group consisting of hinokitiol and salts thereof, and cyclodextrin inclusion compounds containing same, as well as a packaging material for preserving the freshness of the edible materials, which comprises such a synthetic resin film, and a method of preserving the freshness of greens, vegetables and fruit, which comprises packaging or covering the edible materials with a packaging material comprising the synthetic resin film.

In accordance with the present invention, there is also provided a wrapping film comprising (i) a synthetic resin film composed of at least one compound selected from the group consisting of hinokitiol and salts thereof, and cyclodextrin inclusion compound containing the same, and (ii) at least one barrier layer on the outer surface of the synthetic resin film.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

As described above, the synthetic resin film of the present invention comprises at least one compound selected from the group consisting of hinokitiol, salts thereof and cyclodextrin inclusion compounds containing same, and the content of these compounds ranges from 0.1 to 5,000 mg, in terms of the reduced amount of hinokitiol, preferably 0.1 to 2000 mg, more preferably 20 to 300 mg, per 1 m<sup>2</sup> of the film. When the content thereof is less than 0.1 mg/m<sup>2</sup>, a required antibiotic effect cannot be obtained, and when used in an amount of more 5000 mg/m<sup>2</sup>, no substantial significant improvement in the effect is obtained.

As materials for making the synthetic resin films of the present invention, a variety of copolymers or copolymers may be used, but particularly preferred are olefinic polymers. The olefin polymers used herein are, for example, homopolymers of  $\alpha$ -olefins having not more than 12 carbon atoms such as ethylene, propylene, 1-butene, 1-hexene and 3-methyl-1-pentene; random or block copolymers of these  $\alpha$ -olefins; or copolymers comprising an olefin as a principal component and other monomers such as vinyl acetate, acrylic acid, methacrylic acid, alkyl acrylate and/or alkyl methacrylates. Specific examples thereof include high density polyethylene, low density polyethylene, linear low density polyethylene, polypropylene, ethylene/propylene random copolymers, ethylene/propylene rubbers, ethylene/butene-1 rubbers, ethylene/propylene/butene-1 random copolymers, ethylene/propylene block copolymers,

ethylene/propylene/butene-1 block copolymers, ethylene/vinyl acetate copolymers, propylene/butene-1 random copolymers, ethylene/(meth) acrylic acid copolymers and metal salts of ethylene/(meth)acrylic acid copolymers, and these materials may be used alone or in any combination thereof.

In addition to the foregoing olefin polymers, other polymers such as styrene polymers and 1,2-polybutadiene may be used.

As the materials for the barrier layer, any materials having an oxygen barrier property may be used. Typical examples thereof are nylon (i.e., polyamides), partially or totally saponified ethylene-vinyl acetate copolymers, polyethylene terephthalates, oriented polypropylenes, polyvinylidene chlorides, cellophanes, polyvinyl alcohols, as well as the vapor deposition films having deposited thereon, for example, aluminum, silica and metallic foils such as aluminum foils.

The synthetic resin film of the present invention can be prepared by incorporating, into the foregoing olefin polymer, at least one compound selected from the group consisting of hinokitiol and salts thereof, and cyclodextrin inclusion compounds containing same (hereinafter referred to as "hinokitiols") and then forming the resulting compound into a film. The hinokitiols may be incorporated into a monomer mixture prior to the preparation of a polymer, or after the polymerization and before forming into a film. Further, the film may be molded by any conventional method, for example, an extrusion molding such as an inflation molding or T-die molding method.

Examples of the hinokitiols used in the present invention are hinokitiol per se, salts thereof (inclusive of complex salts and double salts thereof) or cyclodextrin inclusion compounds containing hinokitiol or salts thereof.

The synthetic resin film of the present invention is preferably formed from olefin polymers as discussed above, and preferably has a ratio of carbon dioxide (CO<sub>2</sub>) permeability/oxygen (O<sub>2</sub>) permeability of from 2 to 10, more preferably 3 to 7. When greens, vegetables and fruit are packaged with such a film with a ratio of CO<sub>2</sub> permeability/O<sub>2</sub> permeability of less than 2, the concentration of CO<sub>2</sub> in the package increases, and thus the breathing of the packaged vegetables and fruit becomes difficult.

This ratio of the permeabilities can be adjusted by appropriately selecting the thickness of the film. The thickness of the film varies depending on the kind of synthetic resins used, but in general is from 5 to 200μm, preferably 12 to 120μm.

The melt flow rate (MFR determined according to JIS-K 7210) of the synthetic resin used in the present invention is not restricted to a particular level, but preferably the materials used have an MFR value of from 0.1 to 10 g/10 min.

The wrapping films according to the second aspect of the present invention can be prepared by forming a laminated film composed of the above-mentioned synthetic resin film containing hinokitiol therein and a barrier layer laminated on the outer side of the synthetic resin film. The hinokitiols may be incorporated into a monomer mixture prior to the preparation of the polymer, or after the polymerization and before forming into a film. The film may be molded according to any conventionally known method; for example, a co-extrusion molding such as a multilayer-inflation molding or multilayer-T-die molding method. Alternatively, the lamination may be carried out by adhering a barrier layer film to the pre-formed synthetic resin film having the hinokitiols incorporated therein in any conventional manner, such as a dry or wet lamination method or extrusion lamination method, to form the desired multi-laminated wrapping film.

The barrier layer according to the second aspect of the present invention preferably has an oxygen permeability of 3,000 ml/m<sup>2</sup>•24hrs•atm at 23°C or less, more preferably 100 ml/m<sup>2</sup>•24hrs•atm at 23°C or less, determined by a method according to ASTM D3985-81. The thickness of the wrapping film according to the present invention largely varies depending upon various factors, but preferably the thickness of the synthetic resin film is 5 to 200μm and the thickness of the barrier layer is 1 to 100μm.

According to the second aspect of the present invention, the hinokitiol atmosphere can be further maintained for a long period of time due to the presence of the outermost barrier layer. The sustained release effect can be controlled from several hours to 120 days or more, as the barrier layer efficiently prevents the evaporation of the hinokitiols to the outside of the wrapping, and thus the hinokitiols evaporate only into the inside of the wrapping.

The hinokitiols, i.e., hinokitiol, salts thereof or cyclodextrin inclusion compounds containing same, can suppress the development and proliferation of microorganisms, and therefore, the synthetic resin films containing same effectively preserve the freshness of the edible materials packaged with the films. In this respect, the details of the functions and mechanism of this freshness preserving effect of the film have not yet been clearly elucidated, but the sustained release effect of the film is assumed to be involved in these functions and mechanism. Namely, if the hinokitiols are applied to the surface of films, the hinokitiols are correspondingly present on the surface, and thus the volatilization thereof is continued even during the storage and packaging operations, and they are also liable to cause a blooming phenomenon. These

phenomena are greatly affected by the internal environmental conditions in the package. Moreover, it is thus very difficult to arbitrarily control the hinokitiols so that they are gradually released from the film, and to change the release rate depending on the purpose of the application. Conversely, in the present invention, the hinokitiols are dispersed in the film and, therefore, the release rate thereof can be controlled, depending on the purpose of the application, by changing the kind of resin used or the composition of the resin used.

The synthetic resin film or wrapping film of the present invention effectively preserves the freshness of the edible materials, as explained above, and the present invention thus further provides a packaging material for preserving the freshness of the edible materials, which comprises the above-mentioned synthetic resin film.

The packaging material of the present invention is not restricted to a specific shape, and it can be used for preserving or packaging the edible materials in various forms. For example, the material can be used in the form of sheets, bags or a lining of corrugated fibreboard containers or the like. For example, when the material is used in the form of a bag, the freshness of the edible materials can be preserved over a long period of time by sealing one end of a tubular film or three sides of two superimposed sheet-like films, to make a bag, and then introducing the edible materials; or sealing the back and the bottom of a sheet-like material to make a bag and then introducing the edible materials, and finally, sealing the opening of the bag. The term "sealing" herein means heat sealing (heat sealing in a broad sense and inclusive of, for example, impulse heat sealing, high frequency heat sealing and ultrasonic sealing), adhesion (adhesion in a broad sense and inclusive of an adhering method using components other than films and hot melt adhesion), adhesion with tapes, and sealing with a rubber string or ring. Namely, any sealing or closing means may be used as long as the opening of the containers made from films is closely sealed so that little of the air in the container leaks out through the opening, or a complete air-tight condition can be obtained.

Thus, the freshness of the edible materials, especially, greens, vegetables, fruit and processed foods can be preserved over a long time by packaging same with the packaging materials of the present invention, because the hinokitiols are evaporated into the inside of the wrapping, efficiently and under controlled conditions.

When a generation of ethylene from greens, vegetables and fruit is observed, or when a large quantity of water is generated after packaging same with the packaging materials for preserving the freshness of the edible materials according to the present invention, it is possible to simultaneously use conventionally known ethylene absorbers or moisture absorbers, and thus the effect of preserving the freshness thereof can be further enhanced. Furthermore, when a relatively large amount of water (e.g., drips) is generated during the use of the present wrapping materials, any conventional water or moisture absorbers may be used, in combination with the present wrapping material, to further improve the desired freshness preserving abilities.

## EXAMPLES

The present invention will now be further illustrated by, but is by no means limited to, the following Examples.

### Example 1

A linear low density polyethylene L-LDPE (density measured by JIS K7112: 0.924 g/cm<sup>3</sup>; MFR measured JIS K7210 under condition 4: 0.8 g/10 min) containing 0.5% by weight of hinokitiol was inflation molded, under the conditions of an extrusion temperature of 190°C and a take-off speed of 35 m/min, from a 50 mmφ extruder, whereby an inflation film having a lay-flat width of 270 mm and a thickness of 15 μm was obtained. The evaporation rate of the hinokitiol and the quantity thereof evaporated off were determined by using the resulting film (1 m<sup>2</sup>) according to a method of determining the loss of weight. The determination was carried out at a temperature of 23°C and a relative humidity of 60%, and as a result, it was found that the hinokitiol was evaporated off in an amount of 34.5 mg per 1 m<sup>2</sup> of the film after 3 days.

Then, one end of the film was sealed, the film was cut to form a bag having a length of 450 mm, and the bag filled with 1 kg of cherries, to carry out a preservation test at room temperature. As a result, the development of mold, decayed cherries and a browning of the stalk or a wrinkling of the fruit surface were not observed, and further, the fruit was still juicy and had a good appearance even after a lapse of 7 days. Thus, the cherry had a desired commercial value even after 7 days storage.

### Example 2

The same procedures as used in Example 1 were repeated except that 1.0% by weight of hinokitiol was added to the raw polymer to give a film. The loss of hinokitiol through evaporation was 69.0 mg per 1 m<sup>2</sup> of the film.

The same preservation test as performed in Example 1 was carried out, and it was found that, even after a lapse of 7 days, no development of mold, decayed cherries and browning of the stalk, or wrinkling of the fruit surface, were observed and the fruit was still juicy and had a good appearance. Thus, the cherry had a desired commercial value even after 7 days storage.

#### Example 3

Sixty heads of broccoli immediately after harvesting were classified into 5 groups each comprising 12 heads of broccoli, each group was introduced into a film prepared in the same manner as in Example 1, the opening thereof was folded, and the resulting packages were packed in a corrugated fibreboard container.

#### Comparative Example 1

Using a bag prepared in the same manner as in Example 1, except that hinokitiol was not employed, the same preservation test as used in Example 1 was performed. As a result, a development of mold was observed after a lapse of 7 days, and although 65% of the fruit did not have surface wrinkling, was juicy, had a good appearance, and thus had a desired commercial value, the rates of decayed fruit and browning of the stalk were as high as 10% and 25%, respectively.

#### Comparative Example 2

One kg of cherries was introduced into a corrugated fibreboard container, to preserve the fruit. As a result, 10% of the fruit had a wrinkled surface and 10% suffered from browning of the stalk, but no decayed fruit were observed after a lapse of 2 days. After 3 days, the development of mold was observed, and after 7 days, mold was developed over all the area. At this stage, the rates of decayed fruit and browning of the stalk were 30% and 80%, respectively, and thus the fruit had no commercial value at all.

#### Comparative Example 3

One kg of cherries was introduced into a corrugated fibreboard container and then a 500 ppm aqueous solution of hinokitiol was sprayed on the cherries in the form of a mist, to preserve the fruit. After a lapse of 2 days, no development of mold and decayed fruit was observed, but the rate of browning of the stalk was 10% and a wrinkling of the fruit surface was observed. After 7 days, the development of mold was still not observed and no decayed fruit were observed, but the rate of browning of the stalk reached 100%, and thus the fruit had no commercial value at all.

#### Comparative Example 4

Twelve heads of broccoli were packed in a large-sized corrugated fibreboard container and the container was sealed using a gum tape, to carry out a preservation test.

#### Comparative Example 5

Twelve heads of broccoli were packed in a bag of a high-pressure polyethylene having a thickness of 0.03 mm, the opening thereof was folded, and the package was then introduced into a corrugated fibreboard container as in Comparative Example 4, to carry out a preservation test.

#### Comparative Example 6

Twelve heads of broccoli were packed in a film obtained in the same manner as in Comparative Example 1, the opening thereof was folded, and the package was then introduced into a corrugated fibreboard container as in Comparative Example 4, to carry out a preservation test.

#### Comparative Example 7

Twelve heads of broccoli were packed in a corrugated fibreboard container, then SRH-100 (a film of rayon paper having a thickness of 0.15 mm and containing 100 mg/m<sup>2</sup> of hinokitiol) was placed over the broccoli and the container was sealed with a gum tape, to carry out a preservation test.

The thickness, the gas permeabilities and the ratio of the gas permeabilities of the films obtained in Examples 1 and 2 and Comparative Examples 1 and 5 were determined, and the results are summarized in the following Table 1.

Furthermore, in Example 3 and Comparative Examples 4 to 7, the resulting packages were first cooled to 10° C by precooling in vacuo and then stored at room temperature (20 to 23° C). The conditions of the packages were observed every day to examine and confirm the development of mold, smelling and yellowing of the contents of the container. The results are shown in the following Table 2.

Table 1

Ex. No.	Thickness (μm)	Gas Permeability (ml/m <sup>2</sup> •24 hrs•atm• at 23° C)		Ratio of Gas Permeability
		CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub> /O <sub>2</sub>
1	15	27,500	7,900	3.48
2	15	28,000	8,100	3.46

Table 2

Time Elapsed (day)	Items Evaluated	Ex. No.	Comparative Ex. Number				
		3	4	5	6	7	
2	development of mold	-	-	-	-	-	
	smell	-	-	+	-	-	
	yellowing	-	+	-	-	-	
3	development of mold	-	+	+	+	-	
	smell	-	+	+	±	-	
	yellowing	-	+	-	-	±	
4	development of mold	-	+	+	+	-	
	smell	-	*	✱	±	-	
	yellowing	-	+	-	-	±	
5	development of mold	-	+	+	+	-	
	smell	-	*	✱	+	-	
	yellowing	-	+	-	-	+	

\*: putrid smell

✱: smell of acidified product

As seen from the results of the preservation tests for the cherries and broccoli shown in the foregoing Table, the materials according to the present invention preserved the freshness of the vegetables and fruit

better than the comparative materials.

The synthetic resin film of the present invention has a proper ratio of carbon dioxide permeability/oxygen permeability, and thus suppresses the respiration of vegetables and fruit. Moreover, since the film comprises hinokitiol uniformly dispersed therein, the hinokitiol is gradually released over a long time, and thus the effect thereof of inhibiting the proliferation of microorganisms lasts for a long time.

Further, the packaging material for preserving the freshness according to the present invention can sufficiently inhibit the post-ripening phenomenon through the suppression of the respiration of vegetables and fruit packaged with the material, can provide a drastic increase in the effect of inhibiting the proliferation of microorganisms, can extend the storage time of the packaged vegetables and fruit, can minimize the number of pretreatments required after harvesting, and can simplify the packaging operations, and thus can enhance the commercial value of the vegetables and fruit.

Consequently, the present invention can be applied as an effective technique for preserving the freshness of vegetables and fruit, and can be widely used.

#### Example 4

A water-cooled multilayered inflation film having a lay-flat width of 230 mm and an overall thickness of 60  $\mu\text{m}$  (i.e., a layer structure of 20  $\mu\text{m}$  internal layer/20  $\mu\text{m}$  intermediate layer/20  $\mu\text{m}$  outer layer) was formed by a 3-kind 3-layer water-cooling multilayer inflation molding method at a take-off speed of 18 m/min, i.e., by extruding a linear low density polyethylene L-LDPE used in Example 1 containing 0.54% by weight of hinokitiol, as a resin for the internal layer, with a 45 mm $\phi$  extruder A at an extrusion temperature of 190 °C, an adhesive resin (i.e., maleic anhydride-modified L-LDPE), as a resin for the intermediate layer, with a 45 mm $\phi$  extruder B at an extrusion temperature of 185 °C and a nylon resin (i.e., Alamine CM1021-XFS available from Toray Industries, Inc.), as a resin for the outer layer, with a 45 mm $\phi$  extruder C at an extrusion temperature of 240 °C and a die temperature of 250 °C. The content of hinokitiol was determined by collecting 10 cm square of the above-prepared film, extracting the film sample by refluxing the sample with chloroform at 50 °C for 30 minutes, and analyzing the resulting extract by an ultraviolet spectrophotometry, and was found to be 98 mg/m<sup>2</sup>. One end of the above film was closed by heat sealing, the film was then cut to make a bag having a length of 340 mm, and then 1.5 l of air was enclosed in the resulting bag to determine the rate of evaporation of hinokitiol and the loss thereof through evaporation. The determination was carried out under the conditions of a temperature of 23 °C and a relative humidity of 60%. As a result, it was found that hinokitiol was evaporated in the bag in an amount of 0.74 ppm after 30 minutes. Moreover, the barrier property of the above film was found to be 72 ml/m<sup>2</sup>•24 hrs•atm at 23 °C as expressed in terms of the oxygen permeability.

Thereafter, one end of the above film was closed through heat sealing, then the film was cut to make a bag having a length of 200 mm, 25 g of boiled fish paste which had been treated with steam was introduced therein, and the bag was closely sealed to package same in the presence of air. A preservation test was then carried out at 15 °C, and as a result, after a lapse of 8 days, no development of mold, decay, yellowing and surface wrinkling were observed and the fish paste was still juicy and had a good appearance. Thus, the boiled fish paste still maintained a desired commercial value. The standard plate count determined after 8 days was 220,000/g for psychrophilic bacteria (cultured at 21 °C) and 290,000/g for thermophilic bacteria (cultured at 35 °C).

#### Example 5

A film was prepared in the same manner as in Example 4, except that hinokitiol was incorporated in an amount of 0.27% by weight. The content of hinokitiol was determined by collecting 10 cm square of the foregoing film, extracting the film sample by refluxing the sample with chloroform at 50 °C and analyzing the resulting extract by the ultraviolet spectrophotometry, and was found to be 50 mg/m<sup>2</sup>. One end of the foregoing film was closed by heat sealing, the film was then cut to make a bag having a length of 340 mm, and then 1.5 l of air was enclosed in the resulting bag to determine the rate of evaporation of hinokitiol and the loss thereof through evaporation. The determination was carried out under the conditions of a temperature of 23 °C and a humidity of 60%, and as a result, it was found that hinokitiol was evaporated in the bag in an amount of 0.28 ppm after 30 minutes. Moreover, the barrier properties of the foregoing film were found to be 70 ml/m<sup>2</sup>•24 hrs•atm at 23 °C as expressed in terms of the oxygen permeability.

The same preservation test used in Example 4 was carried out using the resulting bag, and as a result, after the lapse of 8 days, no development of mold, decay, yellowing and surface wrinkling was observed, the fish paste was still juicy and had a good appearance. Thus, the boiled fish paste still maintained a



desired commercial value. The standard plate count determined after 8 days was 1,200,000/g for psychrophilic bacteria (cultured at 21 ° C) and 1,000,000/g for thermophilic bacteria (cultured at 35 ° C).

#### Example 6

A film was prepared in the same manner as in Example 4, and the preservation test was carried out under the same conditions as in Example 4, except that the substance to be preserved was vacuum packaged. As a result, after the lapse of 10 days, no development of mold, decay, yellowing and surface wrinkling was observed, and the fish paste was still juicy and had a good appearance. Thus, the boiled fish paste still maintained a desired commercial value. The standard plate count determined after 10 days was 5,900/g for psychrophilic bacteria (cultured at 21 ° C) and 7,400/g for thermophilic bacteria (cultured at 35 ° C).

#### Example 7

A film was prepared in the same manner as in Example 4, and 200 g of fried fish paste (5 pieces in the form of a bar) were packaged with the film to carry out a preservation test. As a result, after the lapse of 5 days, no development of mold, decay, yellowing and surface wrinkling was observed, the fried fish paste was still juicy, had a good appearance, soft resistance to the teeth and a good resiliency. Thus, the fried fish paste still maintained a desired commercial value. The standard plate count determined after 5 days was 33,000/g for psychrophilic bacteria (cultured at 21 ° C) and 20,000/g for thermophilic bacteria (cultured at 35 ° C).

#### Example 8

A film was prepared in the same manner as in Example 4, and raw chicken was packaged with the film to carry out a refrigeration preservation test. The chicken was thawed after 5 days and stored at 1 ° C. As a result, the appearance immediately after the thawing was good and no dripping was observed. Even after 10 days, the appearance was good and no dripping was observed.

#### Comparative Example 8

A bag was prepared in the same manner as in Example 4 except that hinokitiol was not employed. The barrier property of the film constituting the bag was 72 ml/m<sup>2</sup>•24 hrs•atm at 23 ° C as expressed in terms of the oxygen permeability. The preservation test for boiled fish paste which had been steamed was performed under the same conditions as in Example 4, using the resulting bag. As a result, no development of mold was observed, but surface wrinkling was observed, and the fish paste was less juicy and had a relatively low resiliency, and thus had a low commercial value after a lapse of 8 days. The standard plate count determined after 8 days was 16,000,000/g for psychrophilic bacteria (cultured at 21 ° C) and 13,000,000/g for thermophilic bacteria (cultured at 35 ° C).

#### Comparative Example 9

A preservation test was carried out under the same conditions as in Example 4 using a bag prepared by supplying L-LDPE resins free of hinokitiol and extruded under the same conditions as in Example 4. The development of mold and surface wrinkling were observed as a result, it was formed that the steamed fish paste was less juicy and had a relatively low resiliency, and thus a poor commercial value, after the lapse of 8 days. The standard plate count determined after 8 days was 19,000,000/g for psychrophilic bacteria (cultured at 21 ° C) and 17,000,000/g for thermophilic bacteria (cultured at 35 ° C).

#### Comparative Example 10

A bag was prepared in the same manner as in Example 4 except that hinokitiol was not used, and 200 g of fried fish paste (5 pieces in the form of a bar) were packaged in the bag in the presence of air to carry out a preservation test under the same conditions as in Example 4. As a result, the fried fish paste was slightly tough and had a low resiliency, and a bad resistance to the teeth, and thus a bad taste, after the lapse of 5 days. The standard plate count determined after 5 days was 1,900,000/g for psychrophilic bacteria (cultured at 21 ° C) and 1,400,000/g for thermophilic bacteria (cultured at 35 ° C).

### Comparative Example 11

A film was prepared in the same manner as in Example 4 except that hinokitiol was not incorporated, and raw chicken was packaged with the film to carry out a refrigeration preservation test over 5 days. The chicken was thawed after 5 days and stored at 1 °C. As a result, the appearance immediately after the thawing was good and no dripping was observed. After a 5-day-storage, the chicken underwent a slight color change to pale yellow and dripping was observed. After a 10-day-storage, the chicken emitted an offensive smell. Thus, the chicken had no commercial value at all.

As seen from the results of the preservation test for the steamed fish paste, fried fish paste and the raw chicken performed in the foregoing Examples and Comparative Examples, the materials of the present invention preserve the freshness of vegetables and fruit better than the comparative materials.

### Example 9

A linear low density polyethylene L-LDPE used in Example 1 containing 0.5% by weight of hinokitiol was inflation molded under the conditions of an extrusion temperature of 190 °C and a take-off speed of 30 m/min from a 50 mm $\phi$  extruder. Thus, an inflation film having a lay-flat width of 230 mm and a thickness of 20  $\mu$ m was obtained.

The content of hinokitiol was determined by collecting 10 cm square of the above-prepared film, extracting the film sample by refluxing the sample with chloroform at 50 °C for 30 minutes, and analyzing the resulting extract by an ultraviolet spectrophotometry, and was found to be 97 mg/m<sup>2</sup>. One end of the above film was closed by heat sealing, the film was then cut to make a bag having a length of 340 mm, and then 1.5 l of air was enclosed in the resulting bag to determine the rate of evaporation of hinokitiol and the loss thereof through evaporation. The determination was carried out under the conditions of a temperature of 23 °C and a relative humidity of 60%.

As a result, it was found that hinokitiol was evaporated in the bag in an amount of 0.32 ppm after 30 minutes. Moreover, the barrier property of the above film was found to be 7500 ml/m<sup>2</sup>•24 hrs•atm at 23 °C as expressed in terms of the oxygen permeability.

The preservation test was carried out under the same conditions as in Example 4, except that a substance (boiled fish paste) to be preserved was vacuum packaged. The package became loose the next day and after 2 or 3 days, the packaging shape appeared to have the same appearance as in the air-containing package. After the lapse of 8 days, no development of mold and decay was observed, but some surface wrinkling and the decoloration of the boiled fish paste were observed and the resilience thereof was relatively low. The standard plate count determined after 8 days was 4,000,000/g for psychrophilic bacteria (cultured at 21 °C) and 3,000,000/g for thermophilic bacteria (cultured at 35 °C).

The packaging film according to the present invention has a multilayered structure which comprises a synthetic resin film containing at least one compound selected from the group consisting of hinokitiol, salts thereof and cyclodextrin inclusion compounds containing these and at least one barrier layer as an outer layer. Thus, the packaging film comprising, for example, hinokitiol uniformly dispersed therein, has an ability to gradually release hinokitiol or the like, and makes it possible to prevent a dissipation thereof outside the package, due to the presence of the barrier layer, and accordingly, the effect of inhibiting the proliferation of microorganisms lasts for a long time. Moreover, the packaging film makes it possible to evaporate hinokitiol or the like within the package with a high efficiency and under a good control. Therefore, the packaging film can effectively preserve the freshness of, in particular, processed food, in which the control of the respiration of the food is not an essential factor for the preservation of the freshness.

Further, the packaging material for preserving freshness according to the present invention can provide a dramatic increase in the effect of inhibiting the proliferation of microorganisms in the packaged food, can extend the storage time of the packaged foods, can minimize the number of pretreatments required after the preparation thereof, can simplify the packaging operations and can prevent the deterioration of the food, and thus can enhance the commercial value of the foods.

Consequently, the present invention can be applied as an effective technique for preserving the freshness of vegetables and fruit, and can be widely used.

### Claims

1. A synthetic resin film comprising at least one compound selected from the group consisting of hinokitiol and salts thereof and cyclodextrin inclusion compounds containing the same.

2. A synthetic resin film as claimed in claim 1, wherein the film comprises at least one compound selected from the group consisting of hinokitiol and salts thereof and cyclodextrin inclusion compounds containing the same in an amount ranging from 0.1 to 5,000 mg, in terms of the reduced amount of hinokitiol, per 1 m<sup>2</sup> of the film.
- 5 3. A synthetic resin film as claimed in claim 1 or 2, wherein the film has a ratio of carbon dioxide permeability/oxygen permeability of from 2 to 10.
- 10 4. A synthetic resin film as claimed in any one of claims 1 to 3, wherein the synthetic resin is an olefin polymer.
5. A packaging material for preserving a freshness of an edible material, comprising a synthetic resin film according to claim 1.
- 15 6. A method of preserving a freshness of an edible material, comprising packaging or covering said edible material with a synthetic resin film according to claim 1.
- 20 7. A wrapping film comprising (i) a synthetic resin film composed of at least one compound selected from the group consisting of hinokitiol and salts thereof and cyclodextrin inclusion compounds containing the same and (ii) at least one barrier layer on the outer surface of the synthetic resin film.
- 25 8. A wrapping film as claimed in claim 7, wherein the film comprises at least one compound selected from the group consisting of hinokitiol and salts thereof, and cyclodextrin inclusion compounds containing the same in an amount ranging from 0.1 to 5,000 mg, in terms of the reduced amount of hinokitiol, per 1 m<sup>2</sup> of the film.
9. A wrapping film as claimed in claims 7 or 8, wherein the synthetic resin is an olefin polymer.
- 30 10. A wrapping film as claimed in claim 7, wherein the barrier layer has an oxygen permeability of 3,000 ml/m<sup>2</sup>•24hrs•atm at 23° C or less determined by a method according to ASTM D3985-81.
11. A packaging material for preserving a freshness of an edible material, comprising a wrapping film according to claim 7.
- 35 12. A method of preserving a freshness of an edible material, comprising packaging or covering said edible material with a synthetic resin film according to claim 7.

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## EUROPEAN SEARCH REPORT

Application Number

EP 91 10 8440

### DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	WORLD PATENTS INDEX LATEST Week 8747, Derwent Publications Ltd., London, GB; AN 87-331194 (47) & JP-A-62 236 440 (SEIWA KASEI KK) 16 October 1987 * abstract *	1,5-7, 11-12	B65D 81/28
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Y	EP-A-0 180 468 (SEIWA TECHNOLOGICAL LABORATORIES LTD.) * claims 1-33 *	1-12	
D	& JP-A-61 108 359 (SEIWA TECHNOLOGICAL LABORATORIES LTD.)		
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The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
BERLIN	23 JANUARY 1992	ALVAREZ ALVAREZ C.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			