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(11) **EP 1 186 552 A1**

(12) **EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 158(3) EPC

(43) Date of publication:  
**13.03.2002 Bulletin 2002/11**

(51) Int Cl.7: **B65D 77/06, B65D 81/26**

(21) Application number: **00917303.0**

(86) International application number:  
**PCT/JP00/02409**

(22) Date of filing: **13.04.2000**

(87) International publication number:  
**WO 00/63092 (26.10.2000 Gazette 2000/43)**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**

(30) Priority: **16.04.1999 JP 10925299**

(71) Applicant: **KYOWA HAKKO KOGYO CO., LTD.**  
**Chiyoda-ku, Tokyo 100-8185 (JP)**

(72) Inventors:  
• **HAMADA, Shinichirou,**  
**Kyowa Hakko Kogyo Co., Ltd.**  
**Hofu-shi, Yamaguchi 747-8522 (JP)**

- **TOMOHIRO, Susumu,**  
**Kyowa Hakko Kogyo Co., Ltd.**  
**Hofu-shi, Yamaguchi 747-8522 (JP)**
- **FUKUDA, Naoyuki, Kyowa Engineering Co., Ltd.**  
**Chuo-ku, Tokyo 104-0033 (JP)**
- **INOUE, Toshiaki, Kyowa Hakko Kogyo Co., Ltd.**  
**Hofu-shi, Yamaguchi 747-8522 (JP)**
- **SAKAI, Yasuo, Kyowa Hakko Kogyo Co., Ltd.**  
**Chiyoda-ku, Tokyo 100-8185 (JP)**

(74) Representative: **Sajda, Wolf E., Dipl.-Phys. et al**  
**MEISSNER, BOLTE & PARTNER**  
**Postfach 86 06 24**  
**81633 München (DE)**

(54) **PACKING CONTAINER AND PACKING METHOD**

(57) A packaging container which comprises an item packaging bag made of a packaging material having at least one of high moisture permeability and high air permeability for packaging a solid or powder, an inner packaging bag made of a packaging material having at least one of low moisture permeability and low air permeability for containing the item packaging bag, a des-

iccant or oxygen absorber disposed between the item packaging bag and inner packaging bag and an outer packaging container for containing the inner packaging bag as well as a method of packaging which uses the above container.

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**Description**TECHNICAL FIELD

**[0001]** The present invention relates to packaging of a substance which is liable to change in properties or to deteriorate in quality, such as caking or discoloration, under the influence of moisture, oxygen and/or microorganisms.

BACKGROUND ART

**[0002]** In cases where amino acids as raw materials for the production of medicine, or antibiotics or nucleic acid-related substances are stored in containers or shipped as products, those substances are generally packed in bags made of plastics and then packed in outer packaging containers. Thus, they are handled in a doubly packaged condition. In this case, the plastics containers serve as innerpackagingmaterials, and solid containers such as paper drums or metal drums serve as outer packaging materials. Generally, the inside of the paper drums is laminated with aluminum foil in many instances for preventing moisture absorption, and polyvinylidene chloride films, aluminum foil and plastic films having a silica (SiO<sub>x</sub>) deposited layer are known as materials capable of shutting off both moisture and oxygen.

**[0003]** Packaging materials made of plastic films having a metallized or silica (SiO<sub>x</sub>) deposited layer have been used commercially. For instance, Japanese Published Unexamined Patent Application No 100043/99 describes a form of moisture-proof packaging of a massive substance in which an inner packaging material a paperboard drum having a metal-free constitution is used as an outer packaging material and inner packaging material is a film having a silica (SiO<sub>x</sub>) deposited silicon oxide layer. Generally, a polyethylene film or the like is used for item packaging, a film having a silica (SiO<sub>x</sub>) deposited silicon oxide layer or the like is used for inner packaging, and a paper drum is used for outer packaging.

**[0004]** In cases where a substance which is liable to change in properties or deteriorate in quality, such as caking or discoloration, under the influence of moisture, oxygen and/or microorganisms, is packaged in an ordinary form of packaging, the substance change in properties or deteriorate, for example, the substance cakes as a result of growth of microorganisms or is discolored by the action of oxygen.

DISCLOSURE OF INVENTION

**[0005]** An object of the present invention to solve the above problems in prior art and provide a packaging container which can inhibits the growth of microorganisms in the contents and prevents changes in properties or deterioration in quality, such as caking or discoloration, as well as a method packaging using the packaging

container.

**[0006]** Another object of the present invention is to provide a method of maintaining the equilibrium RH (relative humidity) in the packaging container at a level not higher than 60% during storage as well as a method of reducing the oxygen concentration in the packaging container to not more than 0.1%.

**[0007]** A further object of the present invention is to provide a storing method which comprises the use of the above packaging container and the use of the above method of packaging using the packaging container.

**[0008]** The term "storage" or "storing" as used herein means that a substance which is liable to change in properties or deteriorate in quality, such as caking and/or discoloration, under the influence of moisture, oxygen and/or microorganisms (hereinafter such substance is referred to as "object" for short) is packaged after production and is in a hermetically closed condition until opening. Thus, "storage" also includes such a step as transportation after shipment of the product.

**[0009]** The present invention relates to the following (1) to (23).

(1) A packaging container which comprises an item packaging bag made of a packaging material having at least one of high moisture permeability and high air permeability (high permeability packaging material) for packaging a solid or powder, an inner packaging bag made of a packaging material having at least one of low moisture permeability and low air permeability (low permeability packaging material) for containing the item packaging bag, a desiccant or an oxygen absorber disposed between the item packaging bag and inner packaging bag, and an outer packaging container for containing the inner packaging bag.

(2) A packaging container according to the above (1), wherein the high moisture permeability is represented by a moisture transmission rate of not less than 100 g/m<sup>2</sup>-day and the high air permeability is represented by an oxygen transmission rate of not less than 10,000 cc/m<sup>2</sup>-24 hrs·atm.

(3) A packaging container according to the above (1), wherein the low moisture permeability is represented by a moisture transmission rate of not more than 3 g/m<sup>2</sup>-day and the low air permeability is represented by an oxygen transmission rate of not more than 3 cc/m<sup>2</sup>-24 hrs·atm.

(4) A packaging container according to the above (1), wherein the moisture transmission rate of the item packaging bag is not less than 100 g/m<sup>2</sup>-day and the moisture transmission rate of the inner packaging bag is not more than 3 g/m<sup>2</sup>-day.

(5) A packaging container according to the above (1), wherein the oxygen transmission rate of the item packaging bag is not less than 10,000 cc/m<sup>2</sup>-24 hrs·atm and the oxygen transmission rate of the inner packaging bag is not more than 3 cc/m<sup>2</sup>-24

hrs·atm.

(6) A packaging container according to the above (1), wherein the moisture transmission rate of the item packaging bag is not less than 100 g/m<sup>2</sup>·day and the oxygen transmission rate thereof is not less than 10,000 cc/m<sup>2</sup>·24 hrs·atm and the moisture transmission rate of the inner packaging bag is not more than 3 g/m<sup>2</sup>·day and the oxygen transmission rate thereof is not more than 3 cc/m<sup>2</sup>·24 hrs·atm.

(7) A packaging container according to the above (1), wherein the outer packaging container is a container selected from the group consisting of paper drums, plastic drums, corrugated fibreboard boxes and metal cans, or a paper or plastic bag.

(8) A packaging container according to the above (1), wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of moisture, oxygen and/or microorganisms.

(9) A packaging container according to the above (1), wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of at least one microorganism selected from the group consisting of filamentous fungi, bacteria and yeasts.

(10) A packaging container according to the above (1), wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of at least one microorganism belonging to a genus selected from the group consisting of Aspergillus, Cladosporium, Penicillium, Escherichia, Bacillus, Candida and Saccharomyces.

(11) A packaging container according to the above (1), wherein the solid or powder is a substance selected from the group consisting of foods, food additives, medicinal compounds or drugs, material for medicinal compounds or drugs, materials for cosmetics, amino acids, antibiotics and nucleic acid-related substances.

(12) A method of storing a solid or powder which comprises packaging and storing the solid or powder in the packaging container according to any of the above (1) to (11).

(13) A method of packaging a solid or powder which comprises packaging the solid or powder in an item packaging bag made of a packaging material having at least one of high moisture permeability and high air permeability, then packaging the item packaging bag in an inner packaging bag made of a packaging material having at least one of low moisture permeability and low air permeability together with insertion of a desiccant or an oxygen absorber between the item packaging bag and inner packaging bag, closing the inner packaging bag, and packaging the inner packaging bag in an outer packaging container.

(14) A method of packaging according to the above

(13), wherein the high moisture permeability is represented by a moisture transmission rate of not less than 100 g/m<sup>2</sup>·day and the high air permeability is represented by an oxygen transmission rate of not less than 10,000 cc/m<sup>2</sup>·24 hrs·atm.

(15) A method of packaging according to the above (13), wherein the low moisture permeability is represented by a moisture transmission rate of not more than 3 g/m<sup>2</sup>·day and the low air permeability is represented by an oxygen transmission rate of not more than 3 cc/m<sup>2</sup>·24 hrs·atm.

(16) A method of packaging according to the above (13), wherein the moisture transmission rate of the item packaging bag is not less than 100 g/m<sup>2</sup>·day and the moisture transmission rate of the inner packaging bag is not more than 3 g/m<sup>2</sup>·day.

(17) A method of packaging according to the above (13), wherein the oxygen transmission rate of the item packaging bag is not less than 10,000 cc/m<sup>2</sup>·24 hrs·atm and the oxygen transmission rate of the inner packaging bag is not more than 3 cc/m<sup>2</sup>·24 hrs·atm.

(18) A packaging container according to the above (13), wherein the moisture transmission rate of the item packaging bag is not less than 100 g/m<sup>2</sup>·day and the oxygen transmission rate thereof is not less than 10,000 cc/m<sup>2</sup>·24 hrs·atm and the moisture transmission rate of the inner packaging bag is not more than 3 g/m<sup>2</sup>·day and the oxygen transmission rate thereof is not more than 3 cc/m<sup>2</sup>·24 hrs·atm.

(19) A method of packaging according to the above (13), wherein the outer packaging container is a container selected from the group consisting of paper drums, plastic drums, corrugated fibreboard boxes and metal cans or a paper or plastic bag.

(20) A method of packaging according to the above (13), wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of moisture, oxygen and/or microorganisms.

(21) A method of packaging according to the above (13), wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of at least one microorganism selected from the group consisting of filamentous fungi, bacteria and yeasts.

(22) A method of packaging according to the above (13), wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of at least one microorganism belonging to a genus selected from the group consisting of Aspergillus, Cladosporium, Penicillium, Escherichia, Bacillus, Candida and Saccharomyces.

(23) A method of packaging according to the above (13), wherein the solid or powder is a substance selected from the group consisting of foods, food additives, medicinal compounds or drugs, material for

medicinal compounds or drugs, materials for cosmetics, amino acids, antibiotics and nucleic acid-related substances.

**[0010]** In the following, typical embodiments of the invention are described.

**[0011]** As is well known in the art, filamentous fungi can grow in a lower water activity range as compared with bacteria and yeast, however, cannot grow at a water activity of not more than 0.64. At a water activity of 0.65, only special filamentous fungi such as Aspergillus glaucus, called an osmophilic filamentous fungus, can grow. The relation between the water activity and the equilibrium relative humidity (hereinafter referred to as "equilibrium RH") in the packed product is approximately equal to the equation "water activity x 100 = equilibrium RH in packed product". Therefore, it is possible to inhibit the growth of microorganisms by employing a packaging form in which the equilibrium RH in the packed product can be maintained at about 60% or below. When the equilibrium RH in packages is above 60%, microorganisms may possibly grow during storage of certain contents, and the contents may change in properties or deteriorate in quality, such as caking.

**[0012]** As the microorganisms capable of causing changes in properties or deterioration in quality of the object, there may be mentioned microorganisms belonging to a genus selected from the genera Aspergillus, Cladosporium, Penicillium, Escherichia, Bacillus, Candida and Saccharomyces.

**[0013]** In view of the above, for preventing the object from changes in properties or deterioration in quality, it is necessary to maintain the equilibrium RH in the package at 60% or below.

**[0014]** In cases where it is possible that the object is influenced by oxidation during storage, it is desirable that the oxygen concentration in the package during storage is not higher than 0.1%.

**[0015]** The method of packaging according to the present invention is described in the following.

**[0016]** Firstly, the object to be stored is put in an item packaging bag, and the bag is sealed. For the item packaging bag, a packaging material having at least one of high moisture permeability and high air permeability (hereinafter referred to as "high permeability packaging material") is used. Then, the item packaging bag containing the object is placed in an inner packaging bag. For the inner packaging bag a packaging material having at least one of low moisture permeability and low air permeability (hereinafter referred to as "low permeability packaging material") is used. Thereafter, a desiccant or an oxygen absorber is inserted between the item packaging bag and inner packaging bag. Thus, the inner packaging bag contains the desiccant or oxygen absorber between the inner packaging bag and the item packaging bag. Finally, the inner packaging bag is sealed and placed in an outer packaging container.

**[0017]** By inserting the desiccant, the present inven-

tion makes it possible to maintain the equilibrium RH in the package at 60% or below during storage and thereby prevent the object from undergoing changes in quality during storage.

**[0018]** By inserting an oxygen absorber in lieu of the desiccant, the present invention makes it possible to maintain the oxygen concentration at 0.1% or below and thereby prevent the object from changes in quality during storage.

**[0019]** Upon examination of the equilibrium RH in item packages containing a solid or powder as prepared according to the prior art modes of packaging, equilibrium RH values widely range from 10% or below to 90% or above. The present inventors found that this phenomenon depends also on the physical properties of the object. They also found that a higher equilibrium RH in packages allows microorganisms to grow more rapidly or causes changes in properties or deterioration in quality of the object, such as caking or discoloration, in many instances. There are also cases where oxidation by oxygen causes discoloration of the object.

**[0020]** When packaging is made using an oxygen absorber in lieu of a desiccant in the ordinary form of packaging, the oxygen concentration in the package is 16%. Such oxygen concentration can be reduced to 0.1% or below by employing the packaging container or packaging method of the present invention. If the oxygen concentration in package can be reduced to 0.1% or below, it will become possible to prevent the object from changes in properties or deterioration in quality.

**[0021]** The relative humidity (RH) in the package can be measured by inserting a hygrometer into the package. The oxygen concentration in the package can be measured by inserting an oxygen concentration meter into the package.

**[0022]** In the following, the packaging container and packaging method of the present invention are described in more detail.

#### (a) Item packaging

**[0023]** The item packaging material is packaging to wrap the object, and may be made of any of those materials having at least one of high moisture permeability and high air permeability. For example, microporous sheets, microporous films or perforated films made of plastics may be used. There may be mentioned, microporous polypropylene sheets, microporous polyethylene films and perforated plastics films. In cases where the item packaging material is highly permeable to moisture, the moisture transmission rate of the packaging material is not less than 100 g/m<sup>2</sup>-day, preferably not less than 500 g/m<sup>2</sup>-day, more preferably not less than 1,000 g/m<sup>2</sup>-day. In cases where the item packaging material is highly permeable to air, the packaging material is required to have an oxygen transmission rate of not less than 10,000 cc/m<sup>2</sup>-24 hrs-atm, and the material having a higher oxygen transmission rate is more desir-

able.

**[0024]** Further, in case of powder packaging, it is desirable that the packaging material for item packaging have a pore diameter of not larger than 10  $\mu\text{m}$  so that a fine powder fraction may be prevented from leaking out into the inner packaging bag.

#### (b) Desiccant

**[0025]** As the desiccant, any of those substances generally used as desiccants can be used. Specifically, silica gel, calcium chloride, soda lime, silica-alumina desiccants and the like may be used.

#### (c) Oxygen absorber

**[0026]** As the oxygen absorber, any of those substances generally used as oxygen absorbers can be used. Specifically, active metal powders, dithionite salts, vitamin C, iron sulfate, sodium hyposulfite, water-insoluble oxygen-absorbing plastics having a metal-coupling hemoglobin-like structure, and the like may be used.

#### (d) Inner packaging

**[0027]** The inner packaging is packaging to wrap the item packaging. The inner packaging may be made of any of those materials having at least one of low moisture permeability and low air permeability. That is, it may be a low permeable material showing high barrier properties against moisture and /or oxygen. For example, plastic films having a silica ( $\text{SiO}_x$ ) deposited layer, aluminum laminated films and films with an aluminum metallized layer are preferably used. In cases where the inner packaging material has low moisture permeability, the moisture transmission rate of the packaging material is preferably not more than 3  $\text{g}/\text{m}^2\cdot\text{day}$ , more preferably not more than 1  $\text{g}/\text{m}^2\cdot\text{day}$ . In cases where the inner packaging material has low air permeability, the oxygen transmission rate thereof is preferably not more than 3  $\text{cc}/\text{m}^2\cdot 24 \text{ hrs}\cdot\text{atm}$ , more preferably not more than 1  $\text{cc}/\text{m}^2\cdot 24 \text{ hrs}\cdot\text{atm}$ .

#### (e) Outer packaging

**[0028]** The outer packaging material may be any material for wrapping the inner package. As containers for outer packaging, for example, paper drums, plastic drums, corrugated fibreboard boxes and metal cans as well as paper or plastic bags, and the like may be used.

**[0029]** By storing the object packaged by the above method of packaging in an ordinary environment, it is possible to store the object for a prolonged period of time without causing any changes in properties or deterioration.

### BEST MODES FOR CARRYING OUT THE INVENTION

**[0030]** The following examples illustrate the present invention more specifically, however they are not to be construed as limiting of the scope of the present invention.

#### Example 1

**[0031]** (1) A paper drum (diameter 443 mm x height 657 mm) was used as the outer packaging container. A low-moisture-permeable plastic film bag having a silica ( $\text{SiO}_x$ ) deposited layer (width 710 mm, length 1,300 mm, thickness 80  $\mu\text{m}$ , moisture transmission rate: not more than 3  $\text{g}/\text{m}^2\cdot\text{day}$ ) was used as the inner packaging bag. A high-moisture-permeable microporous polypropylene bag (width 700 mm x length 1,300 mm, thickness 200  $\mu\text{m}$ , moisture transmission rate: 10,000  $\text{g}/\text{m}^2\cdot\text{day}$ ) was used as the item packaging bag.

**[0032]** The item packaging bag was filled with 50 kg of L-alanine, one of amino acids. A humidity sensor was inserted approximately into the center of the object L-alanine, and the item packaging bag was closed with a rubber band. The item package was put in the inner packaging bag, together with two bags each containing 500 g of silica gel as a desiccant, which were placed on the top of the item packaging bag. The inner packaging bag was hermetically closed with a rubber band. This inner packaging bag was further placed in the paper drum (outer packaging container), and the paper drum was then covered with a lid.

**[0033]** The thus-packaged paper drum was allowed to stand at room temperature (20 to 25  $^\circ\text{C}$ ), and the RH in the product in the item packaging bag was measured. As a result, the RH just after filling and packaging was not less than 80%, but the RH after 7 days was reduced to 40% and, after 14 days, to 35%. Thus, it was found that the RH can be reduced to 60% or below in about 1 week, at which microorganisms, in particular filamentous fungi, cannot grow. At this time point, attempts were made to isolate microorganisms, in particular filamentous fungi, from L-alanine crystals, however, no filamentous fungi were detected at all. Storage was further continued, and after 6 months, the container was opened, and the object, namely L-alanine crystals, were observed. The crystals were dry and free-flowing, and no caking was observed at all.

#### (2) Comparative Example

**[0034]** A paper drum (diameter 443 mm x height 657 mm) was used as the outer packaging container. A low-moisture-permeable plastic film bag having a silica ( $\text{SiO}_x$ ) deposited silicon oxide layer (width 710 mm, length 1,300 mm, thickness 80  $\mu\text{m}$ , moisture transmission rate: not more than 3  $\text{g}/\text{m}^2\cdot\text{day}$ ) was used as the inner packaging bag. A low-moisture-permeable polypropylene bag (width 700 mm x length 1,300 mm, thickness 80  $\mu\text{m}$ ,

water vapor transmission rate: 4 to 8 g/m<sup>2</sup>-day) was used as the item packaging bag.

**[0035]** The item packaging bag was filled with 50 kg of L-alanine, one of amino acids, a humidity sensor was inserted into the center of the object L-alanine, and the item packaging bag was closed with a rubber band. The item packaging bag was put in the inner packaging bag, together with two bags each containing 500 g of silica gel as a desiccant, which were placed on the top of the item packaging bag. The inner packaging bag was closed with a rubber band. This inner packaging bag was further placed in the paper drum (outer packaging container) and the paper drum was then covered with a lid.

**[0036]** The thus-packaged paper drum was allowed to stand at room temperature (20 to 25 °C), and the RH in the product in the item packaging bag was measured. As a result, the RH 5 days after filling and packaging was not less than 85%, and even the RH after 30 days was not less than 80%.

**[0037]** Storage was further continued, and after 6 months, the container was opened, and the L-alanine crystals were observed. Partial caking of the crystals was observed.

**[0038]** A caked portion was taken out, and attempts were made to isolate microorganisms, in particular filamentous fungi, from L-alanine crystals in the same manner as in Example 1. A large number of filamentous fungi were detected. Upon morphological observation, the microorganisms were identified as filamentous fungi belonging to the genus Penicillium.

#### Example 2

**[0039]** (1) A paper drum (diameter 443 mm x height 657 mm) was used as the outer packaging container. A low-moisture-permeable plastic film bag having a silica (SiO<sub>x</sub>) deposited layer (width 710 mm, length 1,300 mm, thickness 80 μm, moisture transmission rate: not more than 3 g/m<sup>2</sup>-day) was used as the inner packaging bag. A bag (width 700 mm x length 1,300 mm, average moisture transmission rate: 1,000 g/m<sup>2</sup>-day) manufactured by bonding, by heat sealing, one surface of a high-moisture-permeable microporous polypropylene sheet (thickness 200 μm, moisture transmission rate: 10,000 g/m<sup>2</sup>-day) to one surface of a low-density polyethylene film (thickness 80 μm, moisture transmission rate: 4 g/m<sup>2</sup>-day) was used as the item packaging bag.

**[0040]** The item packaging bag was filled with 50 kg of L-threonine, one of amino acids, a humidity sensor was inserted approximately into the center of the object, L-threonine, and the item packaging bag was closed with a rubber band. The item package was put in the inner packaging bag, together with two bags each containing 500 g of silica gel as a desiccant, which were placed on the top of the item packaging bag. The inner packaging bag was closed with a rubber band. This inner packaging bag was further placed in the paper drum

(outer packaging container) and the paper drum was then covered with a lid. The packaged paper drum was allowed to stand at room temperature (20 to 25 °C), and the RH in the product in the item packaging bag was measured. As a result, the RH just after filling and packaging was not less than 80%, but the RH after 7 days was reduced to 36% and, after 14 days, to 31%. Thus, it was found that the RH can be reduced to 60% or below in about 1 week, at which microorganisms, in particular filamentous fungi, cannot grow.

**[0041]** Storage was further continued, and after 6 months, the container was opened, and the object, namely L-threonine crystals, were observed. The crystals were dry and free-flowing, and no caking was observed at all.

#### Example 3

**[0042]** (1) A paper drum (diameter 443 mm x height 657 mm) was used as the outer packaging container. A low-oxygen-permeable plastic film bag having a silica (SiO<sub>x</sub>) deposited layer (width 710 mm, length 1,300 mm, thickness 80 μm, oxygen transmission rate: not more than 1 cc/m<sup>2</sup>·24 hrs-atm) was used as the inner packaging bag. A high-air-permeable nonwoven fabric bag made of high-density polyethylene (width 700 mm x length 1,300 mm, mean thickness 165 μm, air transmission rate: 22S/100 cc) was used as the item packaging bag. In this case, the air permeability of the item packaging bag was too high to be determined in terms of oxygen transmission rate, hence it was expressed in terms of air transmission rate.

**[0043]** The item packaging bag was filled with 50 kg of L-lysine acetate, one of amino acids, and closed with a rubber band. The item package was put in the inner packaging bag, together with five bags of an oxygen absorber (Ageless Z-6000 PT; product of Mitsubishi Gas Chemical Company, Inc) with an absorbency for oxygen of 6,000 ml, which were placed on the top of the item packaging bag. The inner packaging bag was hermetically closed with a rubber band or by heat sealing. This inner packaging bag was further placed in the paper drum (outer packaging container) and the paper drum was then covered with a lid.

**[0044]** The packaged paper drum was allowed to stand in a constant-temperature, constant-humidity room (40 °C, 75% RH), and after 7 days, the sensor portion of an oxygen concentration meter was inserted into the package, and the oxygen concentration was measured. As a result, the oxygen concentration was found to be 0.08%. Storage was further continued, and after 6 months, the container was opened, and the object, namely L-lysine acetate crystals, were observed. The crystals were still white and no change in quality was observed at all.

(2) Comparative Example

**[0045]** A paper drum (diameter 443 mm x height 657 mm) was used as the outer packaging container. A low-oxygen-permeable plastic film bag having a silica ( $\text{SiO}_x$ ) deposited layer (width 710 mm, length 1,300 mm, thickness 80  $\mu\text{m}$ , oxygen transmission rate: not more than 1  $\text{cc}/\text{m}^2\cdot 24 \text{ hrs}\cdot \text{atm}$ ) was used as the inner packaging bag. A low-density polyethylene film bag (width 700 mm x length 1,300 mm, thickness 80  $\mu\text{m}$ , oxygen transmission rate: 1,900  $\text{cc}/\text{m}^2\cdot 24 \text{ hrs}\cdot \text{atm}$ ) was used as the item packaging bag.

**[0046]** The item packaging bag was filled with 50 kg of L-lysine acetate, one of amino acids, and closed with a rubber band. The item package was put in the inner packaging bag, together with five bags of an oxygen absorber (Ageless Z-6000 PT; product of Mitsubishi Gas Chemical Company, Inc), which were placed on the top of the item packaging bag. The inner packaging bag was closed with a rubber band. This inner packaging bag was further placed in the paper drum (outer packaging container), and the paper drum was then covered with a lid.

**[0047]** The packaged paper drum was allowed to stand in a constant-temperature, constant-humidity room (40 °C, 75% RH), and after 7 days, the sensor portion of an oxygen concentration meter was inserted into the package and the oxygen concentration was measured. As a result, the oxygen concentration was found to be 16%. Storage was further continued, and after 6 months, the container was opened, and the object, namely L-lysine acetate crystals, were observed. The crystals were found discolored (pale yellow), and thus a change in quality was observed.

INDUSTRIAL APPLICABILITY

**[0048]** The present invention can provide a packaging container capable of reducing the relative humidity in the item packaging and maintaining the relative humidity in the item packaging at a low level as well as a method of packaging using the packaging container.

**[0049]** The present invention can also provide a packaging container capable of reducing the oxygen concentration in the item packaging and maintaining the oxygen concentration in the item packaging at a low level as well as a method of packaging using the packaging container.

**[0050]** By using the above packaging container and packaging method, it is possible to provide packages which prevent a substance, which is liable to change in properties or quality under the influence of moisture, oxygen and/or microorganisms, from such changes in properties or deterioration during storage.

Claims

1. A packaging container which comprises an item packaging bag made of a packaging material having at least one of high moisture permeability and high air permeability for packaging a solid, an inner packaging bag made of a packaging material having at least one of low moisture permeability and low air permeability for containing the item packaging bag, a desiccant or oxygen absorber disposed between the item packaging bag and inner packaging bag and an outer packaging container for containing the inner packaging bag.
2. A packaging container according to Claim 1, wherein the high moisture permeability is represented by a moisture transmission rate of not less than 100  $\text{g}/\text{m}^2\cdot \text{day}$  and the high air permeability is represented by an oxygen transmission rate of not less than 10,000  $\text{cc}/\text{m}^2\cdot 24 \text{ hrs}\cdot \text{atm}$ .
3. A packaging container according to Claim 1, wherein the low moisture permeability is represented by a moisture transmission rate of not more than 3  $\text{g}/\text{m}^2\cdot \text{day}$  and the low air permeability is represented by an oxygen transmission rate of not more than 3  $\text{cc}/\text{m}^2\cdot 24 \text{ hrs}\cdot \text{atm}$ .
4. A packaging container according to Claim 1, wherein the moisture transmission rate of the item packaging bag is not less than 100  $\text{g}/\text{m}^2\cdot \text{day}$  and the moisture transmission rate of the inner packaging bag is not more than 3  $\text{g}/\text{m}^2\cdot \text{day}$ .
5. A packaging container according to Claim 1, wherein the oxygen transmission rate of the item packaging bag is not less than 10,000  $\text{cc}/\text{m}^2\cdot 24 \text{ hrs}\cdot \text{atm}$  and the oxygen transmission rate of the inner packaging bag is not more than 3  $\text{cc}/\text{m}^2\cdot 24 \text{ hrs}\cdot \text{atm}$ .
6. A packaging container according to Claim 1, wherein the moisture transmission rate of the item packaging bag is not less than 100  $\text{g}/\text{m}^2\cdot \text{day}$  and the oxygen transmission rate thereof is not less than 10,000  $\text{cc}/\text{m}^2\cdot 24 \text{ hrs}\cdot \text{atm}$  and the moisture transmission rate of the inner packaging bag is not more than 3  $\text{g}/\text{m}^2\cdot \text{day}$  and the oxygen transmission rate thereof is not more than 3  $\text{cc}/\text{m}^2\cdot 24 \text{ hrs}\cdot \text{atm}$ .
7. A packaging container according to Claim 1, wherein the outer packaging container is a container selected from the group consisting of paper drums, plastic drums, corrugated fibreboard boxes and metal cans or a paper or plastic bag.
8. A packaging container according to Claim 1, wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality

under the influence of moisture, oxygen and/or microorganisms.

9. A packaging container according to Claim 1, wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of at least one microorganism selected from the group consisting of filamentous fungi, bacteria and yeasts.
10. A packaging container according to Claim 1, wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of at least one microorganism belonging to a genus selected from the group consisting of Aspergillus, Cladosporium, Penicillium, Escherichia, Bacillus, Candida and Saccharomyces.
11. A packaging container according to Claim 1, wherein the solid or powder is a substance selected from the group consisting of foods, food additives, medicinal compounds or drugs, material for medicinal compounds or drugs, materials for cosmetics, amino acids, antibiotics and nucleic acid-related substances.
12. A method of storing a solid or powder which comprises packaging and storing the solid or powder in the packaging container according to any of Claims 1 to 11.
13. A method of packaging a solid or powder which comprises packaging the solid or powder in an item packaging bag made of a packaging material having at least one of high moisture permeability and high air permeability, then packaging the item packaging bag in an inner packaging bag made of a packaging material having at least one of low moisture permeability and low air permeability with a desiccant or oxygen absorber inserted between the item packaging bag and inner packaging bag, closing the inner packaging bag, and packaging the inner packaging bag in an outer packaging container.
14. A method of packaging according to Claim 13, wherein the high moisture permeability is represented by a moisture transmission rate of not less than 100 g/m<sup>2</sup>·day and the high air permeability is represented by an oxygen transmission rate of not less than 10,000 cc/m<sup>2</sup>·24 hrs·atm.
15. A method of packaging according to Claim 13, wherein the low moisture permeability is represented by a moisture transmission rate of not more than 3 g/m<sup>2</sup>·day and the low air permeability is represented by an oxygen transmission rate of not more than 3 cc/m<sup>2</sup>·24 hrs·atm.
16. A method of packaging according to Claim 13, wherein the moisture transmission rate of the item packaging bag is not less than 100 g/m<sup>2</sup>·day and the moisture transmission rate of the inner packaging bag is not more than 3 g/m<sup>2</sup>·day.
17. A method of packaging according to Claim 13, wherein the oxygen transmission rate of the item packaging bag is not less than 10,000 cc/m<sup>2</sup>·24 hrs·atm and the oxygen transmission rate of the inner packaging bag is not more than 3 cc/m<sup>2</sup>·24 hrs·atm.
18. A packaging container according to Claim 13, wherein the moisture transmission rate of the item packaging bag is not less than 100 g/m<sup>2</sup>·day and the oxygen transmission rate thereof is not less than 10,000 cc/m<sup>2</sup>·24 hrs·atm and the moisture transmission rate of the inner packaging bag is not more than 3 g/m<sup>2</sup>·day and the oxygen transmission rate thereof is not more than 3 cc/m<sup>2</sup>·24 hrs·atm.
19. A method of packaging according to Claim 13, wherein the outer packaging container is a container selected from the group consisting of paper drums, plastic drums, corrugated fibreboard boxes and metal cans or a paper or plastic bag.
20. A method of packaging according to Claim 13, wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of moisture, oxygen and/or microorganisms.
21. A method of packaging according to Claim 13, wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of at least one microorganism selected from the group consisting of filamentous fungi, bacteria and yeasts.
22. A method of packaging according to Claim 13, wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of at least one microorganism belonging to a genus selected from the group consisting of Aspergillus, Cladosporium, Penicillium, Escherichia, Bacillus, Candida and Saccharomyces.
23. A method of packaging according to Claim 13, wherein the solid or powder is a substance selected from the group consisting of foods, food additives, medicinal compounds or drugs, material for medicinal compounds or drugs, materials for cosmetics, amino acids, antibiotics and nucleic acid-related substances.



**Amended claims in accordance with Rule 86(2) EPC.**

1. A packaging container which comprises an item packaging bag made of a packaging material having at least one of high moisture permeability and high air permeability for packaging a solid, an inner packaging bag made of a packaging material having at least one of low moisture permeability and low air permeability for containing the item packaging bag, a desiccant or oxygen absorber disposed between the item packaging bag and inner packaging bag and an outer packaging container for containing the inner packaging bag.

2. The container according to Claim 1, wherein the high moisture permeability is represented by a moisture transmission rate of not less than 100 g/m<sup>2</sup>·day and the high air permeability is represented by an oxygen transmission rate of not less than 10,000 cc/m<sup>2</sup>·24 h·atm.

3. The container according to Claim 1 or 2, wherein the low moisture permeability is represented by a moisture transmission rate of not more than 3 g/m<sup>2</sup>·day and the low air permeability is represented by an oxygen transmission rate of not more than 3 cc/m<sup>2</sup>·24 h·atm.

4. The container according to any of Claims 1 to 3, wherein the moisture transmission rate of the item packaging bag is not less than 100 g/m<sup>2</sup>·day and the moisture transmission rate of the inner packaging bag is not more than 3 g/m<sup>2</sup>·day.

5. The container according to any of Claims 1 to 4, wherein the oxygen transmission rate of the item packaging bag is not less than 10,000 cc/m<sup>2</sup>·24 h·atm and the oxygen transmission rate of the inner packaging bag is not more than 3 cc/m<sup>2</sup>·24 h·atm.

6. The container according to any of Claims 1 to 5, wherein the moisture transmission rate of the item packaging bag is not less than 100 g/m<sup>2</sup>·day and the oxygen transmission rate thereof is not less than 10,000 cc/m<sup>2</sup>·24 h·atm and the moisture transmission rate of the inner packaging bag is not more than 3 g/m<sup>2</sup>·day and the oxygen transmission rate thereof is not more than 3 cc/m<sup>2</sup>·24 h·atm.

7. The container according to any of Claims 1 to 6, wherein the outer packaging container is a container selected from the group consisting of paper drums, plastic drums, corrugated fibreboard boxes and metal cans or a paper or plastic bag.

8. The container according to any of Claims 1 to 7, wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in

quality under the influence of moisture, oxygen and/or microorganisms.

9. The container according to any of Claims 1 to 8, wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of at least one microorganism selected from the group consisting of filamentous fungi, bacteria and yeasts.

10. The container according to any of Claims 1 to 9, wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of at least one microorganism belonging to a genus selected from the group consisting of Aspergillus, Cladosporium, Penicillium, Escherichia, Bacillus, Candida and Saccharomyces.

11. The container according to any of Claims 1 to 10, wherein the solid or powder is a substance selected from the group consisting of foods, food additives, medicinal compounds or drugs, material for medicinal compounds or drugs, materials for cosmetics, amino acids, antibiotics and nucleic acid-related substances.

12. A method of storing a solid or powder which comprises packaging and storing the solid or powder in the packaging container according to any of Claims 1 to 11.

13. A method of packaging a solid or powder which comprises packaging the solid or powder in an item packaging bag made of a packaging material having at least one of high moisture permeability and high air permeability, then packaging the item packaging bag in an inner packaging bag made of a packaging material having at least one of low moisture permeability and low air permeability with a desiccant or oxygen absorber inserted between the item packaging bag and inner packaging bag, closing the inner packaging bag, and packaging the inner packaging bag in an outer packaging container.

14. The method according to Claim 13, wherein the high moisture permeability is represented by a moisture transmission rate of not less than 100 g/m<sup>2</sup>·day and the high air permeability is represented by an oxygen transmission rate of not less than 10,000 cc/m<sup>2</sup>·24 h·atm.

15. The method according to Claim 13 or 14, wherein the low moisture permeability is represented by a moisture transmission rate of not more than 3 g/m<sup>2</sup>·day and the low air permeability is represented by an oxygen transmission rate of not more than

3 cc/m<sup>2</sup>·24 h·atm.

**16.** The method according to any of Claims 13 to 15, wherein the moisture transmission rate of the item packaging bag is not less than 100 g/m<sup>2</sup>·day and the moisture transmission rate of the inner packaging bag is not more than 3 g/m<sup>2</sup>·day. 5

**17.** The method according to any of Claims 13 to 16, wherein the oxygen transmission rate of the item packaging bag is not less than 10,000 cc/m<sup>2</sup>·24 h·atm and the oxygen transmission rate of the inner packaging bag is not more than 3 cc/m<sup>2</sup>·24 h·atm. 10

**18.** The method according to any of Claims 13 to 17, wherein the moisture transmission rate of the item packaging bag is not less than 100 g/m<sup>2</sup>·day and the oxygen transmission rate thereof is not less than 10,000 cc/m<sup>2</sup>·24 h·atm and the moisture transmission rate of the inner packaging bag is not more than 3 g/m<sup>2</sup>·day and the oxygen transmission rate thereof is not more than 3 cc/m<sup>2</sup>·24 h·atm. 15 20

**19.** The method according to any of Claims 13 to 18, wherein the outer packaging container is a container selected from the group consisting of paper drums, plastic drums, corrugated fibreboard boxes and metal cans or a paper or plastic bag. 25

**20.** The method according to any of Claims 13 to 19, wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of moisture, oxygen and/or microorganisms. 30 35

**21.** The method according to any of Claims 13 to 20, wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of at least one microorganism selected from the group consisting of filamentous fungi, bacteria and yeasts. 40

**22.** The method according to any of Claims 13 to 21, wherein the solid or powder is a substance which is liable to change in properties and/or deteriorate in quality under the influence of at least one microorganism belonging to a genus selected from the group consisting of Aspergillus, Cladosporium, Penicillium, Escherichia, Bacillus, Candida and Saccharomyces. 45 50

**23.** The method according to any of Claims 13 to 22, wherein the solid or powder is a substance selected from the group consisting of foods, food additives, medicinal compounds or drugs, material for medicinal compounds or drugs, materials for cosmetics, amino acids, antibiotics and nucleic acid-related substances. 55

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/02409

<p>A. CLASSIFICATION OF SUBJECT MATTER Int.Cl<sup>7</sup> B65D77/06, B65D81/26</p> <p>According to International Patent Classification (IPC) or to both national classification and IPC</p>																																		
<p>B. FIELDS SEARCHED</p> <p>Minimum documentation searched (classification system followed by classification symbols) Int.Cl<sup>7</sup> B65D77/04-77/06, B65D81/26</p> <p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000</p> <p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)</p>																																		
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>Y</td> <td>JP, 10-287375, A (Material Eng. Tech. Lab. Inc.), 27 October, 1998 (27.10.98), Full text; Figs. 1 to 4 (Family: none)</td> <td>1-9 11-21 23</td> </tr> <tr> <td>Y</td> <td>JP, 5-319459, A (Mitsubishi Gas Chemical Company, Inc.), 03 December, 1993 (03.12.93), Full text; Figs. 1 to 4 (Family: none)</td> <td>1-9 11-21 23</td> </tr> <tr> <td>Y</td> <td>JP, 63-275345, A (TERUMO CORORATION), 14 November, 1988 (14.11.88), Full text; Fig. 1 &amp; WO, 88008694, A &amp; AU, 1689488, A</td> <td>1-9 11-21 23</td> </tr> <tr> <td>A</td> <td>US, 5086915, A (Terumo Kabushiki kaisha), 11 February, 1992 (11.02.92), Full text; Figs. 1 to 5 &amp; WO, 89005623, A &amp; AU, 1044388, A &amp; EP, 389621, A &amp; KR, 9102559, B &amp; DE, 3751801, C</td> <td>1-23</td> </tr> </tbody> </table> <p><input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.</p> <table border="1"> <tr> <td>* Special categories of cited documents:</td> <td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"E" earlier document but published on or after the international filing date</td> <td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"&amp;" document member of the same patent family</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table> <table border="1"> <tr> <td>Date of the actual completion of the international search 06 July, 2000 (06.07.00)</td> <td>Date of mailing of the international search report 18 July, 2000 (18.07.00)</td> </tr> <tr> <td>Name and mailing address of the ISA/ Japanese Patent Office</td> <td>Authorized officer</td> </tr> <tr> <td>Facsimile No.</td> <td>Telephone No.</td> </tr> </table>		Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	Y	JP, 10-287375, A (Material Eng. 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