



(51) International Patent Classification:

B65D 81/26 (2006.01) *A23B 4/027* (2006.01)
B65D 81/28 (2006.01) *A23L 3/3472* (2006.01)

(21) International Application Number:

PCT/US2013/059858

(22) International Filing Date:

16 September 2013 (16.09.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

13/626,397 25 September 2012 (25.09.2012) US

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier application:

US 13/626,397 (CON)
Filed on 25 September 2012 (25.09.2012)

(71) Applicant: **MULTISORB TECHNOLOGIES, INC.**
[US/US]; 325 Harlem Road, Buffalo, New York 14224-1893 (US).

(72) Inventor: **MCKEDY, George E.**; 261 Oakview Drive, Williamsville, New York 14221 (US).

(74) Agents: **RYAN, Thomas B.** et al.; Harter Secrest & Emery LLP, 1600 Bausch & Lomb Place, Rochester, New York 14604-2711 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: BIOGENIC AMINE ABSORBER

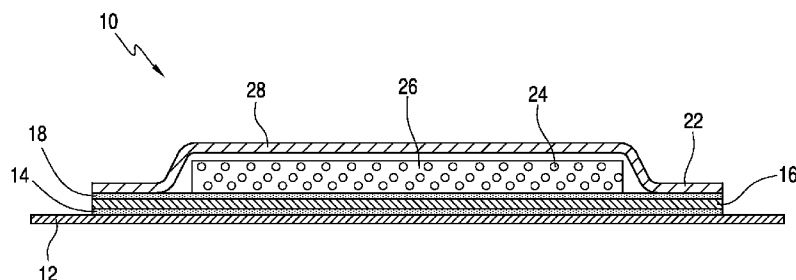


FIG. 1

(57) Abstract: The invention relates to a package for protein containing foods comprising a sealable food covering and, in the interior of the covering, a permeable container wherein an absorbent is in the permeable container and the absorbent comprises an acid that substantially irreversibly reacts with biogenic amines within the covering to form a salt or an amide that is without objectionable odor or toxicity.

BIOGENIC AMINE ABSORBER

FIELD OF THE INVENTION

[0001] This invention relates to the removal of biogenic amines during food storage and packaging.

BACKGROUND OF THE INVENTION

[0002] One of the challenges food packaging industry has to cope with is to preserve packaged goods as long as possible, in order to increase the shelf life of the package. A particular problem is encountered in modified atmosphere packagings (MAP): these packages present a headspace between the packaged good and the packaging film covering the packaged goods, where some unwanted compounds may accumulate during the shelf life. It is known to add additives and substances to packaging films in order to either release substances to the packaged good or to remove substances, either present in the headspace of the packages or generated by the packaged good, from the headspace.

[0003] These so-called active packaging products are for instance capable of removing oxygen, sulfites or aldehydes, from the packaging headspace. U.S. Pat. No. 5,654,061 to Visioli, incorporated herein by reference for all purposes, discloses the incorporation of zeolites into the packaging seal layer in order to adsorb volatile odorous sulfur compounds from the packaging headspace and therefore improve the consumer acceptance of packaged poultry.

[0004] Until recently, fresh fish has been normally transported on ice and then distributed and sold as quickly as possible. Only recently has the packaging of fish in modified atmosphere started. Nevertheless, due to the problem of generation of amines during storage of fish, the packaging of fresh fish is still not common. Although amines generated by bacteria during the aging of fish can be considered as a freshness indicator, they usually smell bad and their accumulation in the headspace of fresh fish packages can lead to rejection by the consumer despite the fact that the fish can still be considered as fresh. In consequence, although the shelf life of fresh fish packaged in MAP can be more than doubled, and more cost effective distribution channels can be used, fresh fish packaging has not yet had the success one could have expected. Removing some of these amines would significantly reduce the number of rejects and extend the shelf life without compromising consumer safety and health.

[0005] Most of the solutions to this problem provided in the art have in common that they require either the addition of a polymer or substance to the package or the incorporation of an additional component into one of the layers of the multilayer film of the flexible film that makes up the package. JP 59-162832 A2 claims the addition of a polymeric substance, e.g. polyacrylate, to a vegetable package to remove bad odor such as amines from the package.

[0006] US 2002/010-6466-Hausmann at A1 discloses the formation of a polymer film comprising up copolymer of ethylene with carboxylic acid to absorb odiferous compounds when packaging materials such as fish.

[0007] Mohan et al. in Food Research International 42 (2009) 411–416 discusses biogenic amine formation in seer fish and the use of oxygen absorbers comprising iron and asorbic acid in combination with chilling to reduce the amines.

[0008] US 5,654,061–Visioli discloses sulfide scavenging packaging materials.

[0009] There is still a need for a package useful for packaging fish or other perishable food items that would remove volatile odiferous compounds, and particularly amines, from inside of the package.

PROBLEM TO BE SOLVED BY THE INVENTION

[0010] There's a need for packaging that will absorb biogenic amines given off by protein such as fish and meat that is packaged for sale. Absorption of these materials will prolong the shelf life of the product.

BRIEF SUMMARY OF THE INVENTION

[0011] The invention provides a package for protein containing foods comprising a sealable food covering and in the interior of the covering a permeable container wherein an absorbent is in the permeable container and the absorbent comprises an acid that substantially irreversibly reacts with biogenic amines in the interior of the covering to form a salt or an amide that is without objectionable odor or toxicity.

[0012] In another embodiment invention provides a food package comprising a sealed food covering, a protein containing food in the covering,

and a permeable container in the covering, wherein an absorbent is in the permeable container and the absorbent comprises an acid that substantially irreversibly reacts with biogenic amines to form a salt or an amide that is without objectionable odor or toxicity.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Figure 1 is cross-sectional schematic view of a label or patch with absorbent of the invention.

[0014] Figure 2 is a cross-sectional schematic of a sachet containing the biogenic amines absorber of the invention.

[0015] Figure 3 is a schematic view of an invention package utilizing the biogenic amines absorber in a label.

[0016] Figure 4 is a schematic cross-sectional view of the use of a biogenic amine absorber sachet in package.

DETAILED DESCRIPTION OF THE INVENTION

[0017] The invention has numerous advantages over the prior art. The invention provides a method of increasing the shelf life of protein rich foods such as meat and fish at low-cost while generally using present packaging and present preservation techniques. Materials of the invention are safe and prevent the formation of toxins in stored meat and fish. The materials of the invention have the advantage that they may be presented in the food packaging art in a way that is familiar to the art and readily carried out in protein packaging. The invention increases the safety of stored foods while

preserving their taste. These and other advantages will be apparent from the drawings and detailed description below.

[0018] In Fig 1 is a schematic illustration of an absorber patch or label for biogenic amines. The patch would be adhered to the inside of a covering forming a food package. The patch 10 is comprised of a removable base 12 of a strippable material that will not adhere significantly to adhesive layer 14. The layer 16 is the support for the patch. Layer 18 provides an adhesive layer for heat sealing the cover layer 28 around its edges 22. Cover layer 28 is permeable to gases but not liquids and attached to layer 18 at its edges 22. This type of label or patch is generally disclosed in US patent 6,139,935-Cullen where the formation of oxygen absorbing labels are disclosed. The formation of label or patch of the instant invention is similar except that the absorbent material is suitable for absorbing biogenic amines not for absorbing oxygen. Iron is not present in the invention bioamine absorber. The acid absorber for biogenic amines 24 is shown as particles within a fibrous material 26 such as filter paper. The acid material may be either a solid acid particle or may be an acid absorbed onto a carrier such as filter paper, activated carbon or molecular sieve material. It is noted that although the particles are shown as embedded in a fibrous material is possible that the acid could be a liquid that is absorbed onto the fibrous material or solid particles could be placed under cover 22 as loose particles. These particles could be an acid material or they could be acid carried by the carrier material such as activated carbon or molecular sieve material. The acid particles may require water for activation.

[0019] Illustrated schematically in cross-section Fig 2 is a sachet 30 that could be used in a package as a biogenic amines absorber. The sachet 30 has a cover 32 which is water impermeable and gas permeable. The sachet is sealed at 34 and 36, and formed from either a tubular sheet member or flat sheet that has been folded over and sealed to form a tube. The tube is filled with the biogenic amine absorber prior to both of the ends being sealed. The absorber shown as particles 38 which may be a solid acid or an acid absorbed onto a carrier such as cellulose, activated carbon or molecular sieve particles. The acid also could be absorbed in or scattered in a cellulose member such as the cellulose member 26 utilized in Figure 1.

[0020] Figure 3 is a package 40 for preparing a protein material such as fish 46 for display or shipping prior to sale. The package comprises a covering 42 that is the outer covering of the package. The covering comprises a bag 42 that is sealed shut at 48. The package 48 has a patch or label 10 fastened to the surface of the covering bag 42. The fish is carried in tray 44. After the fish 46, tray 44, and patch 10 have been placed into the covering it is sealed at 48. While illustrated as having the large space for gas the bag would likely be subjected to vacuum or a modified atmosphere in the bag to lower oxygen content to slow decay and result in closely wrapped fish or other protein material. Conventional packing cannot eliminate oxygen coming from the protein and some decay is caused by enzymes. The biogenic amine absorber 10 will absorb amines given off by the fish and lengthen the time when the fish is suitable for consumer use as it does not have significant odor.

[0021] Figure 4 is a schematic cross-section of a package 50 for fish or other protein with biogenic amines given off from this protein being absorbed by sachet 30. With the exception of the use of the sachet instead of the patch or label 10 the Figure 4 package is similar to the Figure 3 package.

[0022] While the permeable container of the invention that holds the biogenic amines absorber has been illustrated as either a sachet 30 or a label or patch 10 the invention is not limited to these particular containers for biogenic amine absorbers. The container also could be a permeable tube or a container that has one permeable side. It further could be formed of a polymer strip that had biogenic amines absorber embedded in the strip.

[0023] The covering used in the package may be any polymer material that provides good oxygen barrier properties for the food inside. Typical of such materials are polycarbonate, and polyvinyl alcohols, lactic acid polymers, polyesters and polypropylene. A preferred material is polyethylene, particularly low density polyethylene because it is low in cost and has good barrier properties.

[0024] The covering for the package may be wrapped onto the package and sealed, it may be a bag that is sealed, or may be a tube that is sealed at both ends. The formation of sealed air tight food packages is well known.

[0025] The water impermeable air permeable covering for at least a portion of the sachet, container or label of the invention may be any material that will pass the amines and inhibits passage of water or other liquids.

Typical of such materials are microporous spun bonded materials and microporous materials formed by stretching a voided material. A preferred material is a spun bonded polyolefin material such as the well-known Tyvek trademark material.

[0026] Biogenic amines such as trimethylamine are synthesized by decaying animal, plant and enzymatic metabolisms, and consequently are found in a wide variety of food products. Biogenic amine formation is initially the result of protein breakdown. Biogenic amines are related to food safety and food quality issues, as some biogenic amines are associated with several acute adverse reactions in consumers. All protein rich foods subjected to the conditions that allow bacterial development and activity are expected to accumulate certain amounts of biogenic amines. Biogenic amines are in fresh meats, fresh meat products, cooked meat products, cured meat products and fermented meat products. Biogenic amines are also found in chesses, tofu, alcoholic beverages, chocolate, sour cream, yogurt, beans, peas, sauerkraut, some fruits, some nuts, and fish. Some of the biogenic amines are trimethylamine, tyramine, tryptamine, phenylamine, histamine, putrescine, phenylethylamine, agmatine, spermidine, spermine and cadaverine. Fish has been rejected by taste panels in the range of 3.0 – 9.5 mg / 100. grams (3 – 9.5 ppm) of trimethylamine in fish.

Trimethylamine gives fish the pungent fishy odor. The human odor detection threshold of trimethylamine is .00026 – 2.1 mg / m³ (.00026 – 2.1 ppm). Because the threshold of detection is so low, this unpleasant odor becomes apparent long before the wholesomeness of the food is compromised. It is desirable therefore to reduce the biogenic amine odor

so that the product is not rejected by the consumer prematurely. This is why common culinary practice is to sprinkle lemon juice on a fish fillet, for instance, or to serve a wedge of lemon for the diner's use if they want to reduce the fishy odors.

[0027] The packages of the invention will reduce the biogenic amine to below the level a human finds unpleasant and off-putting. For a closely wrapped fish the absorbers of the invention will reduce the biogenic amines after 7 days of refrigerated storage to a level that is acceptable to consumers. The level is suitably less than 10 ppb biogenic amine. A preferred level of less than 3 ppb is obtainable for a closely wrapped piece of fish after 7 days refrigerated storage. Closely wrapped means not baggy or loose. The gas space is less than the protein space in a closely wrapped package. For biogenic amines given off by foods, other than fish, amounts of greater than 5 ppb are not objectionable and greater amounts of these biogenic amines are acceptable to the consumer.

[0028] Any non-toxic acid may be utilized in this invention. Suitable acids are hydrochloric acid, acetic acid, fumaric acid, malic acid, lactic acid, tartaric acid, sorbic acid, terephthalic acid, benzoic acid, adipic acid, and sulfuric acid. A preferred acid is citric acid as it is very effective and safe in foods.

[0029] Any amount of acid may be used that is effective in a particular package. The amount of acid needed varies with the type of protein packages as well as how much protein is packaged.

[0030] An objective of the invention is to formulate an irreversible absorber and reactant that will absorb and react with the biogenic amines that are formed, eliminating the off taste and off odor of the food thereby increasing the shelf life and quality of the food product. The reactant could be used alone or dissolved in water and adsorbed onto an adsorbent such as activated carbon, silica gel, molecular sieve, vermiculite, cellulose paper and absorbent polymers. This would allow the biogenic amine to be irreversibly adsorbed and neither the food product or consumer would not be in contact with the actual reactant.

[0031] Amines react with acids to form ammonium salts. The nonbonded electron pair on the nitrogen bonds the hydrogen ion. If an amine is insoluble the reaction with the acid produces a water soluble salt. Citric acid reacts with the trimethylamine to form a water soluble salt. Along with ammonia, primary and secondary amines yield amides with carboxylic acids. The amides formed may undergo hydrolysis in either an acid or base to form amides, ammonium salts and carboxylic acids.

[0032] The invention utilizes a substantially irreversible biogenic amine adsorber. Amines are to a considerable extent irreversibly adsorbed on hydrated silica gel and aluminum oxide surfaces. When trimethylamine is reacted with citric acid, the citric acid gives its proton to trimethylamine forming $(\text{CH}_3)_3\text{NH}^+$. Trimethylamine is a stronger base than water because nitrogen is less electronegative than oxygen. The trimethylammonium cation is a weaker acid (more stable) than the hydronium ion because nitrogen is less electronegative than oxygen and therefore can accommodate

a positive formal charge more effectively. This trimethylammonium will be stable in the package and does not have an objectionable smell.

EXAMPLES

[0033] The following examples are illustrative but not exhaustive of embodiments of the invention. Parts and percentages are by weight unless otherwise indicated.

[0034] In Examples 1–13 an 11 X 16 inch foil laminated pouch was used to test efficacy of the biogenic amine adsorbers. Inside of the foil pouch was placed a small Tyvek packet with the adsorber material along with a moisture source which was .4 grams of water on blotter paper. If the adsorber was dissolved in water then the adsorber was put on blotter paper inside of a packet and placed inside of the foil pouch with the moisture source. This foil pouch was then vacuumed, heated sealed and filled with three liters of gas containing 10 ppm of trimethylamine. Blank foil pouches were also filled with the trimethylamine containing gas to be used as a standard. The blanks were determined to contain 12,000 and 13,000 ppb trimethylamine for the 7 day test at room temperature. For the 15 day test the blanks were determined to contain 4,500 and 5,200 ppb of trimethylamine at room temperature at the beginning of the test. After 7 days or 15 days an outside analytical laboratory measured the trimethylamine content of the foil pouch. The analytical method used was microextraction gas chromatography mass spectroscopy. 5 ppb is the detection limit of the analytical method for trimethylamine.

[0035] The following are some of the test results:

[0036] Example 1

0.1 gram (.0005 moles) of dry citric acid in a packet reduced the trimethylamine content to less than 5 ppb in the 7 days at room temperature.

[0037] Example 2

.2 grams (.0010 moles) of dry citric acid in a packet without a moisture source reduced the trimethylamine content to 670 ppm in 7 days at room temperature.

[0038] Example 3

.2 grams (.0010 moles) of citric acid in .4 grams of water on blotter paper reduced the trimethylamine content to less than 5 ppb in 7 days at room temperature.

[0039] Example 4

.1 gram (.0005 moles) of citric acid in .2 grams of water on blotter paper reduced the trimethylamine content to less than 5 ppb in 7 days at room temperature.

[0040] Example 5

.2 grams (.0010 moles) of citric acid in .4 grams of water on blotter paper reduced the trimethylamine content to less than 5 ppb in 7 days at room temperature.

[0041] Example 6

.2 grams (.0010 moles) of citric acid in .4 grams of water impregnated on .4 grams of activated carbon reduced the trimethylamine content to less than 5 ppb in 7 days at room temperature.

[0042] Example 7

10.8 grams of .5N hydrochloric acid (.0054 moles) on blotter paper reduced the trimethylamine content to less than 5 ppb in 7 days at room temperature.

[0043] Example 8

5.0 grams of vinegar on blotter paper (5 % acetic acid / .0042 moles) reduced the trimethylamine content to less than 5 ppb in 7 days at room temperature.

[0044] Example 9

.1 gram (.0005 moles) of citric acid blended with .7 grams of sodium chloride reduced the trimethylamine content to less than 5 ppb in 7 days at room temperature.

[0045] Example 10

0.2 grams (.0017 moles) of fumaric acid reduced the trimethylamine content to less than 5 ppb in 7 days at room temperature.

[0046] Example 11

0.2 grams (.0015 moles) of malic acid reduced the trimethylamine content to less than 1,500 ppb in 7 days at room temperature.

[0047] Tests were set up for Examples 12–26 where various biogenic amine adsorber chemistries were tested in the 3 liter vessel that was vacuumed and then filled with 3 liters of gas that contained 10,000 ppb (10 ppm) of trimethylamine in nitrogen. The test was conducted at 4° C (refrigerated temperature) with the following levels of trimethylamine measured after 11 days.

[0048] With respect to Examples 12–22 below the results are listed on the right for Examples 12–26 and these results are after 11 days at 4° C. The initial test vessels are filled with 3 liters of gas containing 10,000 ppb (10 ppm) of trimethylamine. The reaction is slower at colder temperatures and this is the reason that some of the trimethylamine levels are relatively high but they have been reduced from the original 10,000 ppb. The two blank test vessels contained 9,400 ppb and 10,000 ppb of trimethylamine when measured after the 11 days at 4° C. Examples 27–32 use the same test vessels as Examples 12–26, but use different storage temperatures.

[0049] Example 12

.1 gram of citric acid (.0005 moles)	4,700. ppb of trimethylamine
--------------------------------------	------------------------------

[0050] Example 13

.2 grams of citric acid (.0010 moles)	2,200. ppb of trimethylamine
---------------------------------------	------------------------------

[0051] Example 14

.2 grams of citric acid (.0010 moles) dissolved in .4 grams of water and impregnated onto 1.3 grams of activated carbon 1,800. ppb of trimethylamine

[0052] Example 15

.2 grams of citric acid (.0010 moles) dissolved in .4 grams of water and impregnated onto 1.5 grams of silica gel 1,300. ppb of trimethylamine

[0053] Example 16

10.8 grams of .5 N hydrochloric acid (.0054 moles) 820. ppb of trimethylamine

[0054] Example 17

5.0 grams of vinegar (acetic acid) (.0042 moles) less than 5. ppb of trimethylamine

[0055] Example 18

.2 grams of fumaric acid (.0017 moles) 740. ppb of trimethylamine

[0056] Example 19

.3 gram of malic acid (.0022 moles) 490. ppb of trimethylamine

[0057] Example 20

.3 grams of lactic acid (.0033 moles) 1,800. ppb of trimethylamine

[0058] Example 21

.3 grams of tartaric acid (.0020 moles) less than 5. ppb trimethylamine

[0059] Example 22

.3 grams of sorbic acid (.0027 moles) 1,100. ppb trimethylamine

[0060] Example 23

.3 grams of terephthalic acid (.0018 moles) 6,600. ppb trimethylamine

[0061] Example 24

.3 grams of benzoic acid (.0025 moles) 2,100. ppb trimethylamine

[0062] Example 25

.3 grams of adipic acid (.0021 moles) 4,800. ppb trimethylamine

[0063] Example 26

5.0 grams of 1N sulfuric acid (.00025 moles) 1,000. ppb trimethylamine

[0064] Example 27

.001 grams of citric acid (.0000052 moles) reduced the trimethylamine content from 11,500. ppb to 540 ppb of trimethylamine at room temperature in 9 days.

[0065] Example 28

.01 grams of .5 Normal hydrochloric acid .0000052 moles reduced the trimethylamine content from 11,500 ppb to 490 ppb of trimethylamine at room temperature in 9 days.

[0066] Example 29

.2 grams of citric acid reduced the trimethylamine content from 9,350 ppb to 195 ppb in one day, to 115 ppb in 3 days and to 180 ppb in 7 days at room temperature but this same amount of .2 grams of citric acid at refrigerated temperatures reduced the trimethylamine content to 1,450 ppb in one day, 685 ppm in 3 days and to 605. ppb after 7 days.

[0067] Example 30

.45 grams of citric acid (.00234 moles) reduced the trimethylamine content from 10,000 ppb to less than 5. ppb at room temperature in 10 days. At refrigerated temperatures this same amount of time. Citric acid reduced the trimethylamine content to 3,000 ppb.

[0068] Example 31

4.68 grams of .5 Normal hydrochloric acid (.00234 moles) reduced the trimethylamine content form 10,000 ppb at room temperature to less than 5. ppb at room temperature over 10 days. At refrigerated temperatures this same amount of .5 Normal hydrochloric acid reduced the trimethylamine content to less than 5. ppb in the same 10 days.

[0069] Example 32

3.12 grams of .5 Normal hydrochloric acid (.00156 moles) reduced the trimethylamine content from 10,000 ppb at room temperature to less than 5. ppb in 10 days. At refrigerated temperatures this same amount of .5 normal hydrochloric acid reduced the trimethylamine content to less than 5 ppb.

[0070] The above Examples show the effectiveness of a variety of acids. The preferred materials are citric acid and acetic acid for effectiveness with a lesser weight of acid.

[0071] The invention has been described in detail with particular reference to a presently preferred embodiment, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention. The presently disclosed embodiments are therefore considered in all respects to be illustrative and not restrictive. The scope of the invention is indicated by the appended claims, and all changes that come within the meaning and range of equivalents thereof are intended to be embraced therein.

CLAIMS

1. A package for protein containing foods comprising a sealable food covering and, in the interior of the covering, a permeable container wherein an absorbent is in the permeable container and the absorbent comprises an acid that substantially irreversibly reacts with biogenic amines within the covering to form a salt or an amide that is without objectionable odor or toxicity.

2. The package of claim 1 wherein the biogenic amine in the covering consists of at least one member selected from the group of trimethylamine, tyramine, tryptamine, phenylamine, histamine, tryptamine, phenylamine, putrescine, phenylethylamine, agmatine,, spermidine, spermine, and cadaverine.

3. The package of claim 1 wherein the acid comprises hydrochloric acid.

4. The package of claim 1 wherein the acid consists of at least one member selected from the group of citric acid, acetic acid, fumaric acid, malic acid, and sulfuric acid.

5. The package of claim 1 wherein the absorbent is sufficient to reduce biogenic amines to less than 10 ppb when a closely wrapped 4 ounce piece of fish is stored at 40° for seven days.

6. The package of claim 1 wherein the absorbent is sufficient to reduce biogenic amines to less than 5 ppb when a closely wrapped 4 ounce piece of fish is stored at 40° for seven days.
7. The package of claim 1 wherein the acid is absorbed onto a carrier consisting of at least one of activated carbon, silica gel, feldspar and molecular sieve.
8. The package of claim 1 wherein the food covering comprises a moisture impermeable polymer sheet.
9. The Package of claim 1 wherein the permeable container is a gas permeable but water impermeable container.
10. The package of claim 9 wherein the permeable container is a sachet.
11. The package of claim 1 wherein the acid is absorbed onto a carrier.
12. The package of claim 1 wherein the permeable container is adhered to the inside of the food covering.
13. A food package comprising a sealed food covering, a protein containing food in the covering, and a permeable container in the covering, wherein an absorbent is in the permeable container and the absorbent comprises an acid that substantially irreversibly reacts with biogenic amines to form a salt or an amide that is without objectionable odor or toxicity.

14. The package of claim 13 wherein the biogenic amine in the covering consists of at least one member selected from the group of trimethylamine, tyramine, tryptamine, phenylamine, histamine, tryptamine, phenylamine, putrescine, phenylethylamine, agmatine,, spermidine, spermine, and cadaverine.

15. The package of claim 13 wherein the acid comprises hydrochloric acid.

16. The package of claim 13 wherein the acid consists of at least one member selected from the group of citric acid, acetic acid, fumaric acid, malic acid, and sulfuric acid.

17. The package of claim 13 wherein the absorbent is sufficient to reduce biogenic amines to less than 10 ppb when a 4 ounce piece of fish is stored at 40° for seven days.

18. The package of claim 13 wherein the absorbent is sufficient to reduce biogenic amines to less than 5 ppb when a 4 ounce piece of fish is stored at 40° for seven days.

19. The package of claim 13 wherein the acid is absorbed onto a carrier consisting of at least one of activated carbon, silica gel, feldspar and molecular sieve.

20. The package of claim 13 wherein the food covering comprises a moisture impermeable polymer sheet.

21. The Package of claim 13 wherein the permeable container is gas permeable but water impermeable container.

22. The package of claim 21 wherein the permeable container is a sachet.

23. The package of claim 13 wherein the acid is absorbed onto a carrier.

24. The package of claim 13 wherein the permeable container is adhered to the inside of the food covering.

1/2

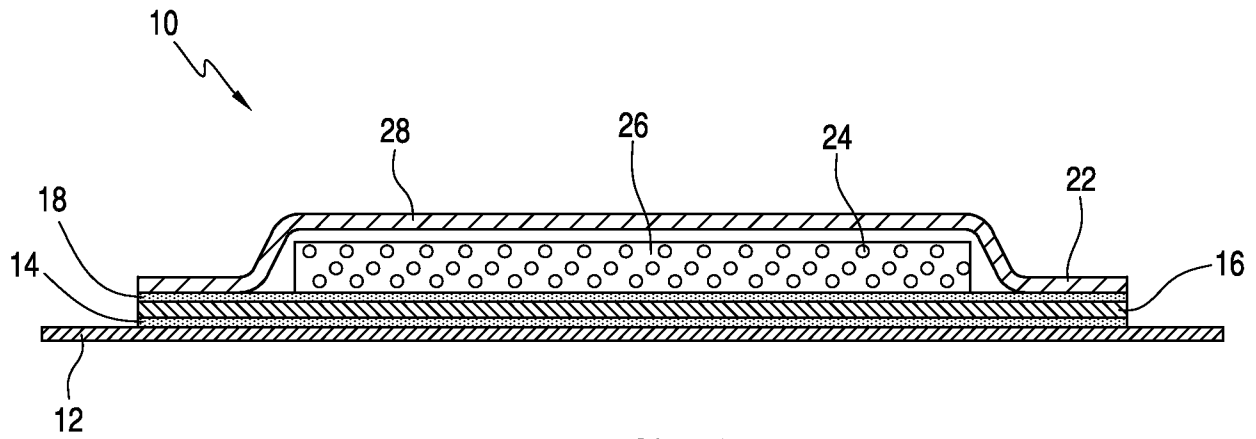


FIG. 1

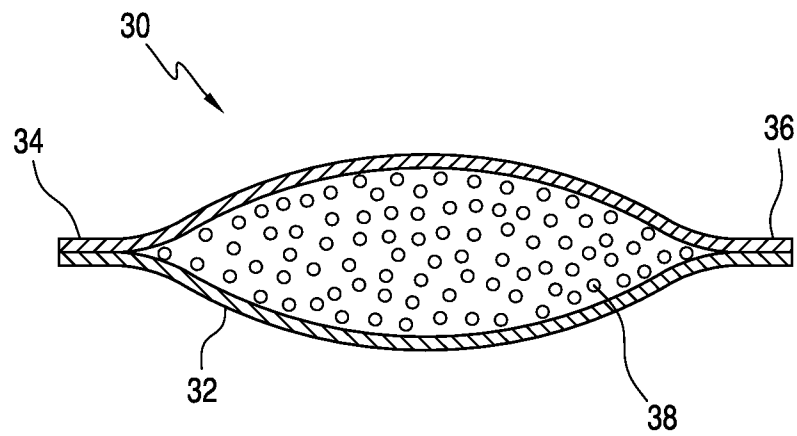


FIG. 2

2/2

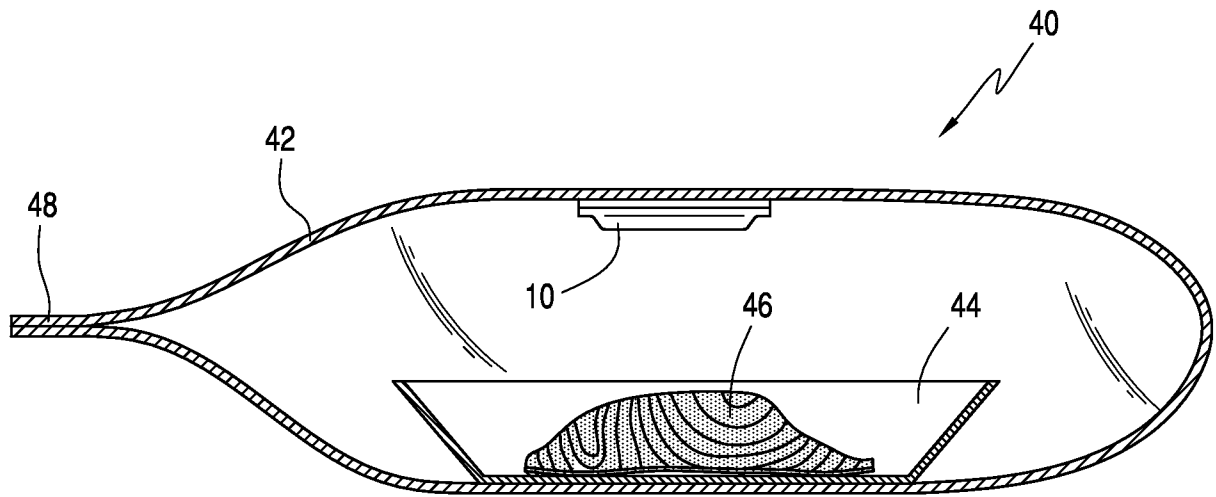


FIG. 3

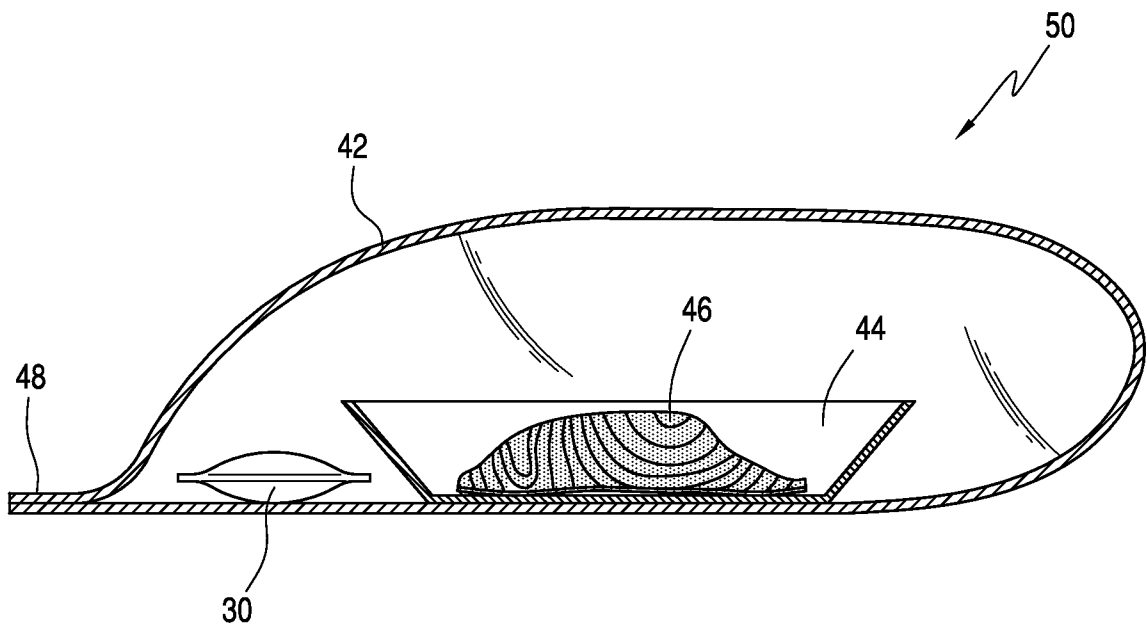


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/059858**A. CLASSIFICATION OF SUBJECT MATTER****B65D 81/26(2006.01)i, B65D 81/28(2006.01)i, A23B 4/027(2006.01)i, A23L 3/3472(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B65D 81/26; B32B 1/04; B29C 67/20; B32B 1/02; B65D 65/42; B65D 85/00; A23L 3/00; B65D 81/28; A23B 4/027; A23L 3/3472

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & keywords: package, protein, food, absorbent, biogenic amines, and acid

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2005-143402 A (SEIKE, KAZUNORI) 9 June 2005 See abstract, paragraphs [0008],[0009], and claim 1.	1-4, 12-16, 24
A		5-11, 17-23
A	US 5654061 A (VISIOLI, DONNA LYNN) 5 August 1997 See column 4, lines 27-39 and claims 1,2.	1-24
A	US 2002-0039610 A1 (POCKAT et al.) 4 April 2002 See paragraphs [0034],[0036], claim 1, and figure 1.	1-24
A	US 2002-0106466 A1 (HAUSMANN et al.) 8 August 2002 See paragraphs [0013],[0017] and claim 1.	1-24
A	US 5833894 A (LANZANI et al.) 10 November 1998 See column 4, line 31 - column 5, line 18 and figures 1-3.	1-24



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

09 December 2013 (09.12.2013)

Date of mailing of the international search report

09 December 2013 (09.12.2013)

Name and mailing address of the ISA/KR

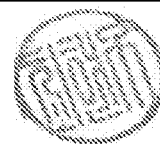
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City,
302-701, Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

CHOI, Hyun Goo

Telephone No. +82-42-481-8288



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/059858

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2005-143402 A	09/06/2005	None	
US 5654061 A	05/08/1997	EP 0830203 A1 EP 0830203 A1 EP 0830203 B1 JP 03564143 B2 JP 11-509135 A KR 10-1999-0022570 A WO 96-22160 A1 WO 96-40429 A1	25/03/1998 11/04/2001 29/01/2003 08/09/2004 17/08/1999 25/03/1999 25/07/1996 19/12/1996
US 2002-0039610 A1	04/04/2002	CA 2346151 A1 US 2004-0175517 A1 US 6709687 B2	02/11/2001 09/09/2004 23/03/2004
US 2002-0106466 A1	08/08/2002	EP 1309400 A2 JP 2004-506555 A WO 02-16221 A2 WO 02-16221 A3	14/05/2003 04/03/2004 28/02/2002 12/09/2002
US 5833894 A	10/11/1998	EP 0754632 A1 EP 0754632 B1	22/01/1997 07/10/1998