US 20140087034A1

(19) **United States**

(12) **Patent Application Publication**

McKedy

(10) **Pub. No.: US 2014/0087034 A1**

(43) **Pub. Date: Mar. 27, 2014**

(54) **BIOGENIC AMINE OXIDIZER OR UNREACTIVE ABSORBER**

(71) Applicant: **MULTISORB TECHNOLOGIES, INC.**, Buffalo, NY (US)

(72) Inventor: **George E. McKedy**, Williamsville, NY (US)

(73) Assignee: **Multisorb Technologies, Inc.**, Buffalo, NY (US)

(21) Appl. No.: **13/626,506**

(22) Filed: **Sep. 25, 2012**

Publication Classification

(51) **Int. Cl.**

B65D 81/26	(2006.01)
B65D 81/20	(2006.01)

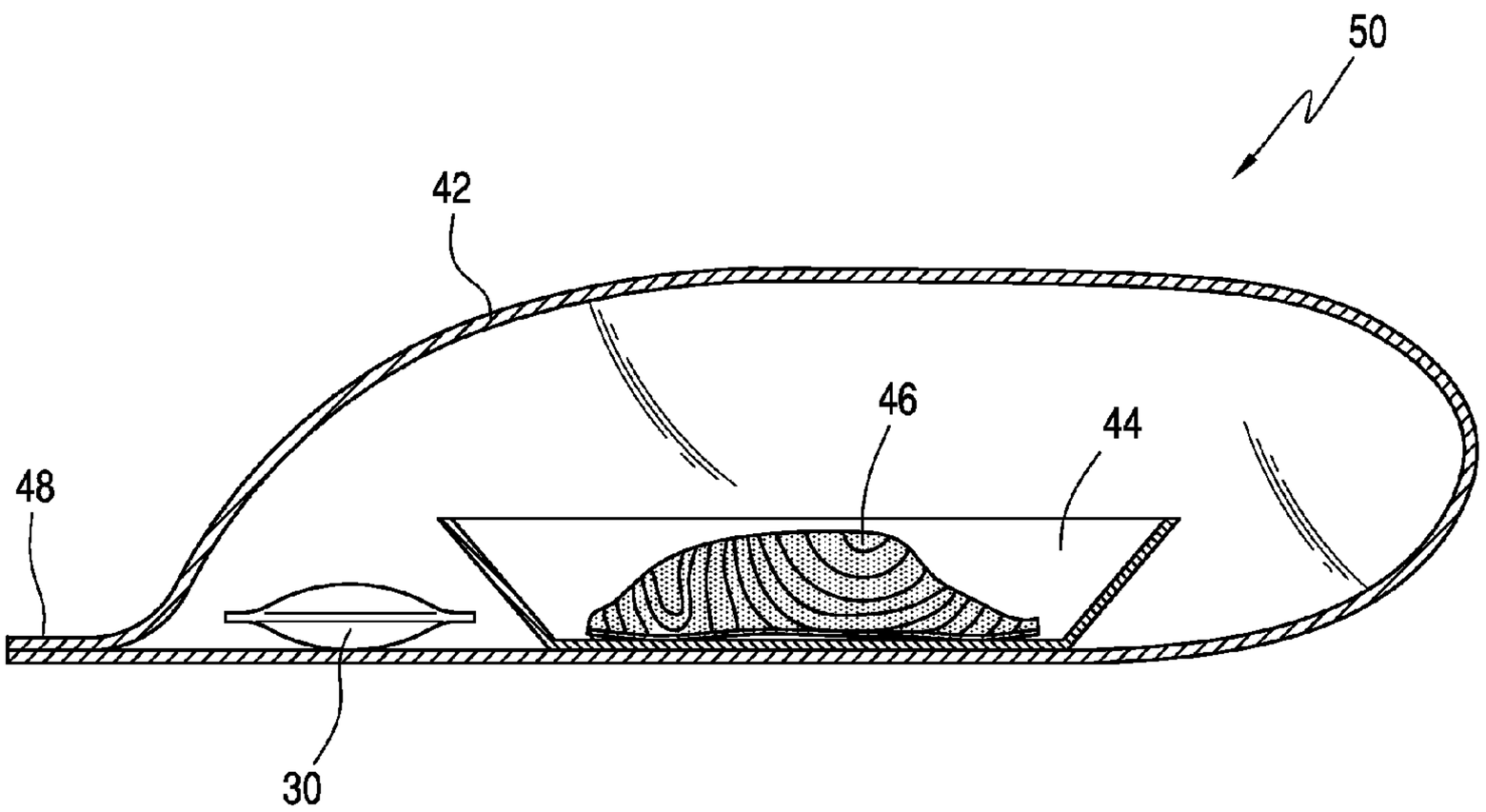
(52) **U.S. Cl.**

CPC ***B65D 81/268*** (2013.01); ***B65D 81/2084*** (2013.01)

USPC **426/124**; 426/129; 206/204

(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 oxidizer is in the permeable container oxidizer substantially irreversibly reacts with biogenic amines within the covering to form compounds without objectionable odor or toxicity; in another embodiment 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 unreactive absorbent is in the permeable container and the unreactive absorbent absorbs, but does not react with biogenic amines within the covering to largely remove the biogenic amines from the package.



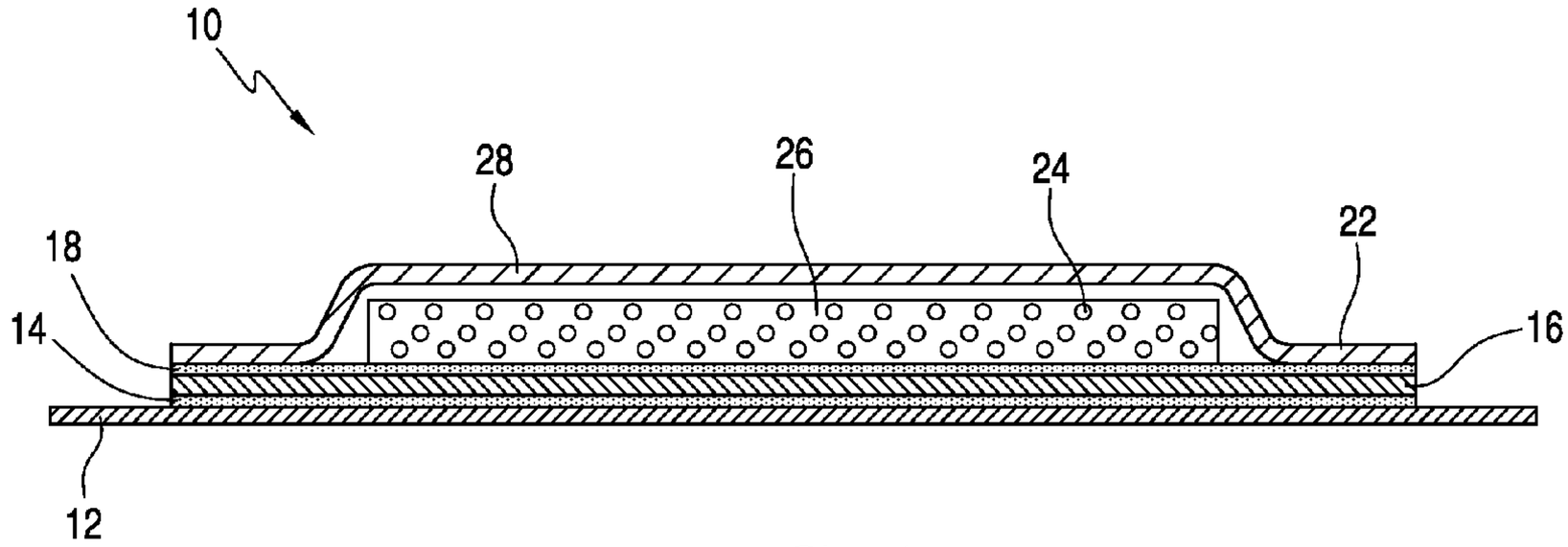


FIG. 1

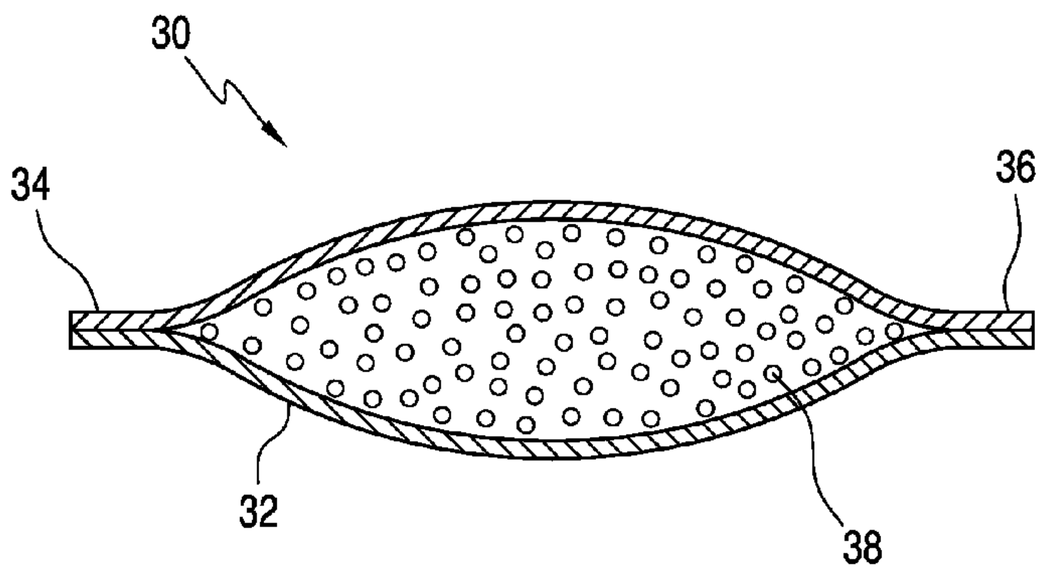


FIG. 2

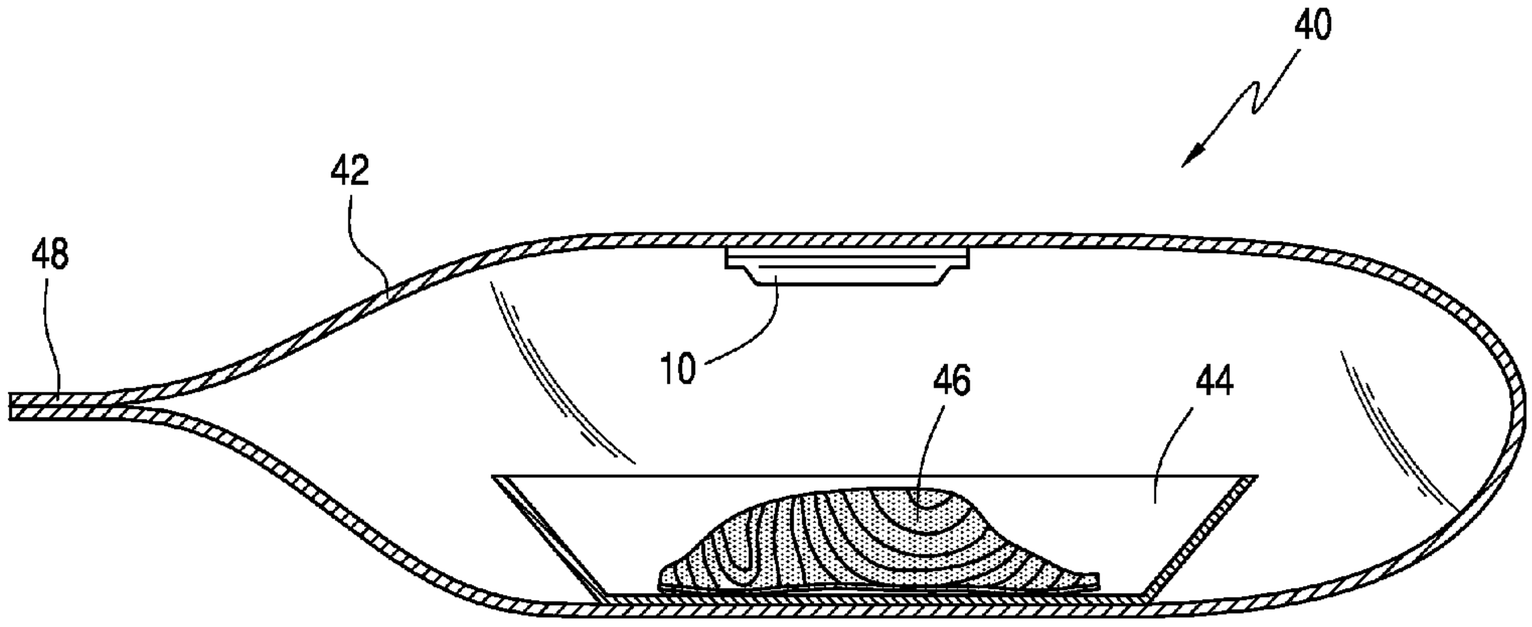


FIG. 3

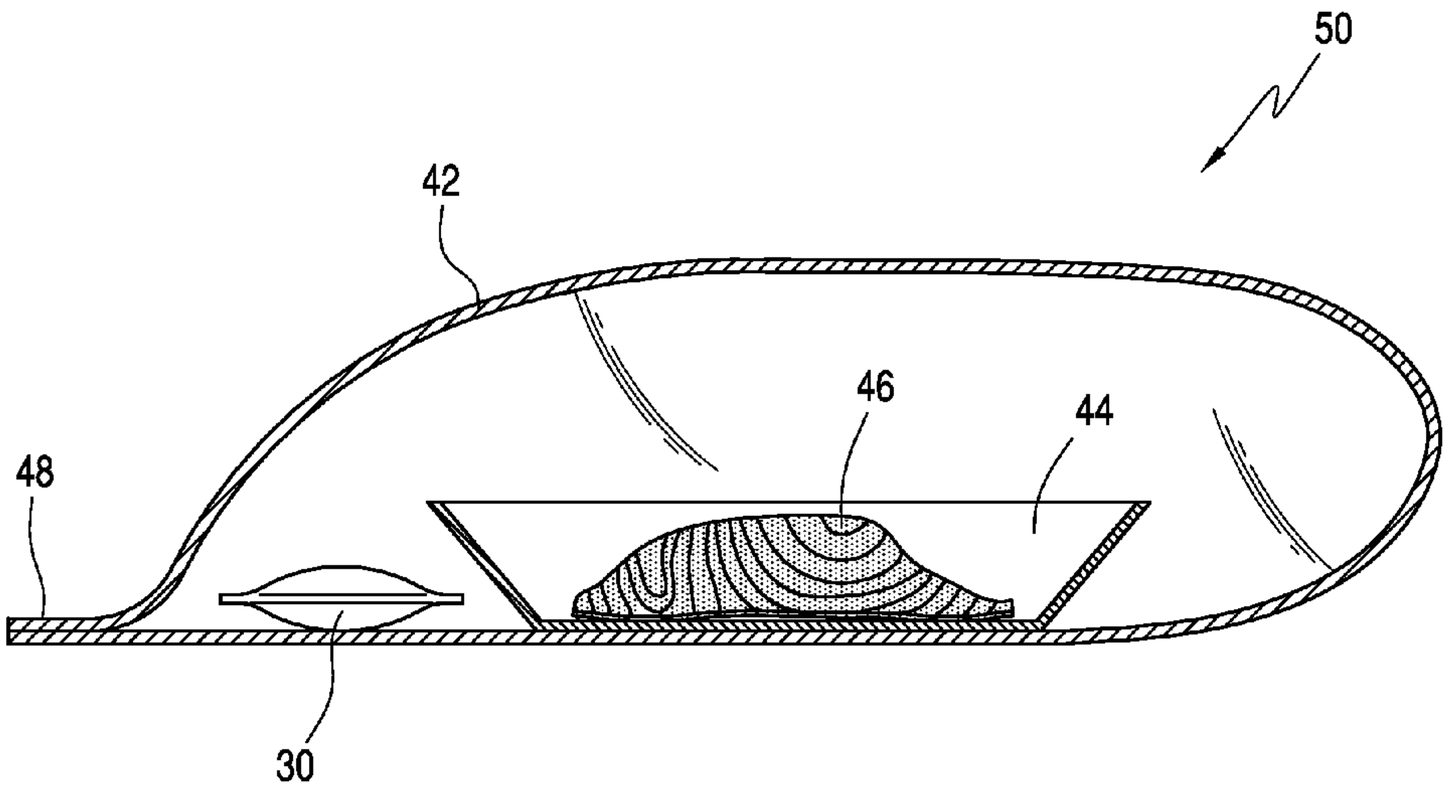


FIG. 4

BIOGENIC AMINE OXIDIZER OR UNREACTIVE 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 packagings 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 Al 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 citric acid in combination with chilling to reduce the amines.

[0008] U.S. Pat. No. 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 oxidizer is in the permeable container oxidizer substantially irreversibly reacts with biogenic amines within the covering to form compounds without objectionable odor or toxicity.

[0012] In another embodiment 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 unreactive absorbent is in the permeable container and the unreactive absorbent absorbs, but does not react with biogenic amines within the covering to largely remove the biogenic amines from the package.

BRIEF DESCRIPTION OF THE DRAWINGS

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

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

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

[0016] FIG. **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 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] 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 U.S. Pat. No. 6,139,935-Cullen where the formation of oxygen absorbing labels is 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. The unreactive or oxidizing absorber for biogenic amines **24** is shown as particles within a fibrous material **26** such as filter paper. The material may be either a solid particle such as activated carbon or molecular sieve for the solid particle or may be an oxidizer such as hydrogen peroxide absorbed onto a carrier such as filter paper. It is noted that although the particles are shown as embedded in a fibrous material the oxidizers such as hydrogen peroxide would be a liquid that is absorbed onto the fibrous material. Solid particles of activated carbon could be placed under cover **22** as loose particles. Generally, it is preferred that solid particles be held in some sort of material to prevent their dispersal if their container is ripped.

[0019] In another embodiment, the invention includes a biogenic releasable absorbing composition including an absorber that will releasably retain the biogenic amine and an oxidizer that will react with the biogenic amine to irreversibly retain the biogenic amine. The oxidizer will react with the biogenic amine to convert the biogenic amine into another compound that cannot later be released back into the package. In operation, the releasable absorber draws the biogenic amine into the composition and the oxidizer absorber reacts with the biogenic amine to form a new compound from which the biogenic amine is not released.

[0020] The releasable absorber may be any substance that will releasably retain the biogenic amine. The releasable absorber preferably is a porous structure that allows for retention of the biogenic amine in its pores. Releasable absorbers usable in the invention include, but are not limited to, activated carbon and silica gel.

[0021] The releasable absorber may remove the biogenic amine from a headspace of a container. However, the releasable absorber can lead to subsequent release of the biogenic amine. Thus, preferred embodiments of the invention utilize an oxidizer material that irreversibly reacts with the biogenic amine.

[0022] 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 activated carbon or molecular sieve particles. An oxidizer such as hydrogen peroxide could be absorbed in a fibrous absorbent cellulose member such as the cellulose member **26** utilized in FIG. **1**.

[0023] FIG. **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 unreactive 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. Unreactive absorbers will absorb biogenic amines, but do not react with the biogenic amine. The unreactive absorbers will largely remove biogenic amines from the consumer package. By "largely remove" it is meant that the biogenic amines are not objectionable to the consumer when the package is opened. The level of biogenic amines not objectionable will vary depending on the particular protein being stored and what biogenic amine is being given off.

[0024] FIG. **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 FIG. **4** package is similar to the FIG. **3** package.

[0025] 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 strip.

[0026] 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.

[0027] 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.

[0028] 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.

[0029] 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, phenylethylaminne, 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 0.00026-2.1 mg/m3 (0.00026-2.1 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.

[0030] 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 ppm 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 much less that the protein space in a closely wrapped package. For biogenic amines given off by foods, other than fish, amounts somewhat greater than 5 ppb are not objectionable and greater amounts of these biogenic amines are acceptable to the consumer.

[0031] The oxidizer may be any material that will oxidize biogenic amines from the atmosphere. Typical of such oxidizers are hydrogen peroxide, sodium chlorite, sodium perchlorate, sodium chlorate, sodium hypochlorite, calcium hypochlorite, sodium chlorate, and potassium permanganate. The preferred oxidizers are hydrogen peroxide and sodium chlorite as they rapidly oxidize vaporous biogenic amines and are safe for use with foods.

[0032] Any unreactive biogenic amine absorber may be utilized that it is substantially unreactive with biogenic amines. Typical of such materials are activated carbon, silica gel, molecular sieve and clay. Suitable materials are molecular sieve and feldspar. Preferred nonreactive absorbers are activated carbon and silica gel as they absorb biogenic amines in high amounts and are safe for use with foods.

[0033] Any amount of unreactive absorbent or oxidizer may be used that is effective in a particular package. The amount needed varies with the type of protein packages and the absorber as well as how much protein is packaged.

[0034] An objective of the invention is to formulate an unreactive absorber or oxidizer for biogenic amine absorbers 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 oxidizer could be used alone or adsorbed onto an adsorbent such as blotting paper. This would allow the biogenic amine to be irreversibly adsorbed and neither the food product nor consumer would not be in contact with the actual reactant. The hydrogen peroxide could be absorbed in an unreactive absorber particle such as activated carbon or silica gel.

EXAMPLES

[0035] The following examples are illustrative but not exhaustive of embodiments of the invention. Parts and percentages are by weight unless otherwise indicated.

[0036] In Examples 1-13 an 11×16 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 0.4 grams of water on blotter paper. If the adsorber was a liquid oxidizer such as hydrogen peroxide 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.

[0037] The following are test results:

Example 1

[0038] 2.0 grams of dry activated carbon with a moisture source reduced the trimethylamine content to 870 ppb in 7 days at room temperature.

Example 2

[0039] 2.0 grams of dry activated carbon without a moisture source reduced the trimethylamine content to less than 5 ppb in 7 days at room temperature.

Example 3

[0040] 2.0 grams of 13× molecular sieve reduced the trimethylamine content to less 1,400 ppb in 7 days at room temperature.

Example 4

[0041] 2.0 grams of 300 angstrom silica gel impregnated with 0.5 grams of moisture reduced the trimethylamine content to less than 5 ppb after 7 days at room temperature.

Example 5

[0042] 2.0 grams of 13× molecular sieve reduced the trimethylamine content to 8 ppb in 15 days at room temperature.

Example 6

[0043] 2.0 grams of 300 angstrom silica gel impregnated with 0.5 grams of water reduced the trimethylamine content to less than 5 ppb in 15 days at room temperature.

Example 7

[0044] 6.6 grams of 3% hydrogen peroxide (0.0058 moles) on blotter paper reduced the trimethylamine content to 16 ppb in 15 days at room temperature.

Example 8

[0045] 0.7 grams of 35% hydrogen peroxide (0.0072 moles) on blotter paper reduced the trimethylamine content to 100 ppb in 15 days at room temperature.

Example 9

[0046] 0.5 grams of sodium chlorite reduced the trimethylamine content to less than 5 ppb in 7 days at room temperature.

[0047] The above Examples show the effectiveness of a variety of unreactive absorbers and oxidizers.

[0048] 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.

1. A package for protein containing foods comprising a sealable food covering and, in the interior of the covering, a permeable container wherein an oxidizer is in the permeable container oxidizer substantially irreversibly reacts with biogenic amines within the covering to form compounds 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 oxidizer comprises hydrogen peroxide or sodium chlorite.

4. The package of claim **1** wherein the oxidizer present 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.

5. The package of claim **1** wherein the oxidizer 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.

6. The package of claim **1** wherein the oxidizer is absorbed onto a carrier consisting of at least one of activated carbon, silica gel, clay and molecular sieve.

7. The package of claim **1** wherein the permeable container is a gas permeable but water impermeable container.

8. The package of claim **7** wherein the permeable container is a sachet.

9. The package of claim **1** wherein the oxidizer is absorbed onto a carrier.

10. The package of claim **1** wherein the permeable container is adhered to the inside of the food covering.

11. A food package comprising a sealed food covering, a protein containing food in the covering, and a permeable container in the covering, wherein an oxidizer is in the permeable container and the oxidizer substantially irreversibly reacts with biogenic amines to form compounds without objectionable odor or toxicity.

12. The package of claim **11** 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.

13. The package of claim **11** wherein the oxidizer comprises hydrogen peroxide or sodium chlorite.

14. The package of claim **11** wherein the oxidizer 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.

15. The package of claim **13** wherein the oxidizer is absorbed onto a carrier consisting of at least one of activated carbon, silica gel, clay and molecular sieve.

16. The Package of claim **11** wherein the permeable container is gas permeable but water impermeable container.

17. The package of claim **16** wherein the permeable container is a sachet.

18. The package of claim **11** wherein the permeable container is adhered to the inside of the food covering.

19. A package for protein containing foods comprising a sealable food covering and, in the interior of the covering, a permeable container wherein an unreactive absorbent is in the permeable container and the unreactive absorbent absorbs, but does not react with biogenic amines within the covering to largely remove the biogenic amines from the package.

20. The package of claim **19** 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.

21. The package of claim **1** wherein the unreactive absorbent comprises activated carbon or molecular sieve.

22. The package of claim **19** wherein the unreactive 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.

23. The package of claim **19** wherein the permeable container is a gas permeable but water impermeable container.

24. The package of claim **7** wherein the permeable container is a sachet.

25. The package of claim **19** wherein the permeable container is adhered to the inside of the food covering.

26. A food package comprising a sealed food covering, a protein containing food in the covering, and a permeable container in the covering, wherein an unreactive absorbent is in the permeable container and the unreactive absorber absorbs, but does not react with biogenic amines to largely remove biogenic amines from the package.

27. The package of claim **19** 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.

28. The package of claim **19** wherein the unreactive absorbent comprises activated carbon or molecular sieve.

29. The package of claim **19** wherein the oxidizer 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.

30. The Package of claim **19** wherein the permeable container is gas permeable but water impermeable container.

31. The package of claim **30** wherein the permeable container is a sachet.

32. The package of claim **19** wherein the permeable container is adhered to the inside of the food covering.

* * * * *