

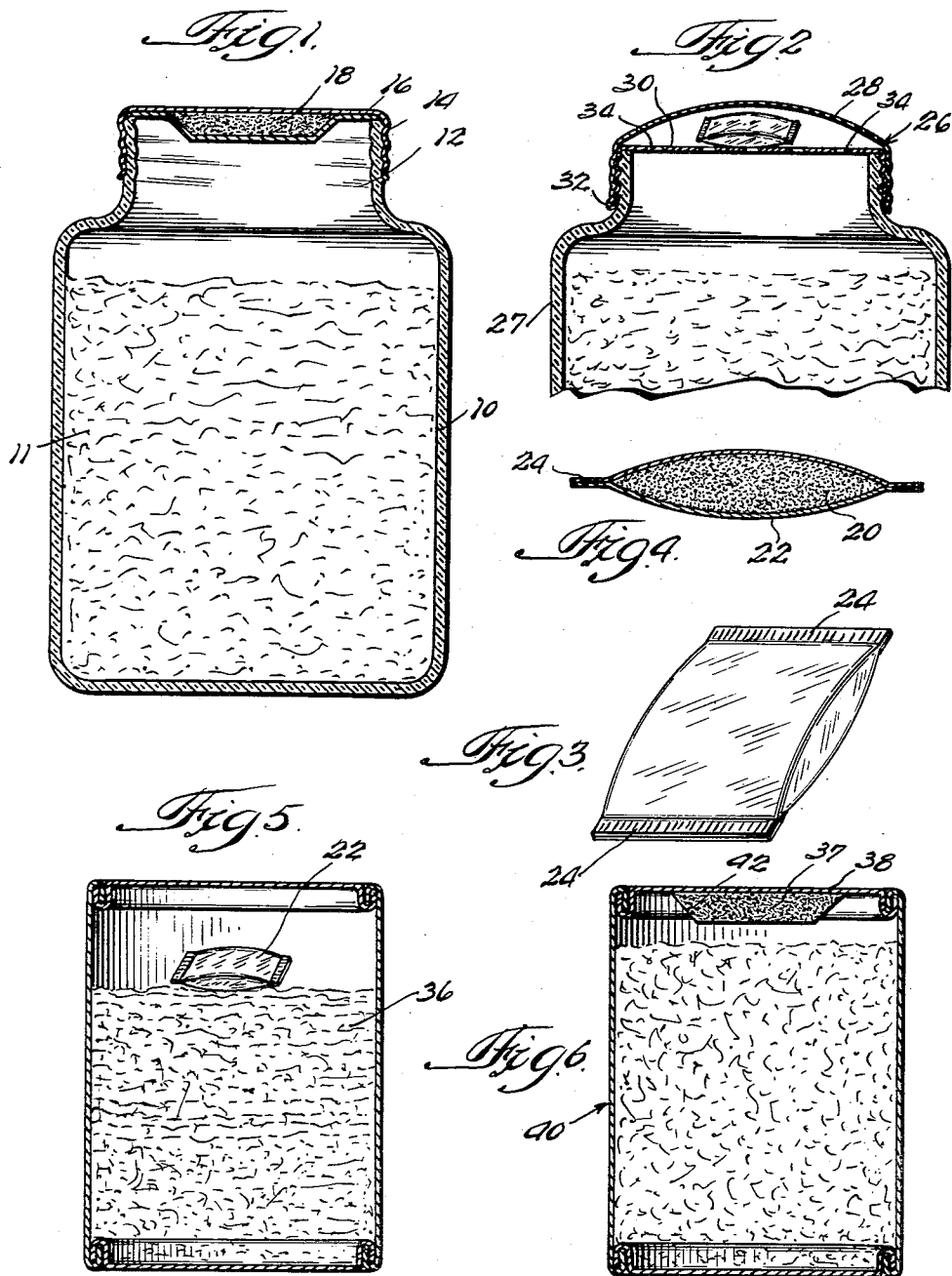
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D. SCOTT

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DEOXYGENATING PROCESS AND PRODUCT

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INVENTOR.

Don Scott.

BY

Thiss, Okar, Mucklenburg,
von Holst, & Coltrane. *Attys.*

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DEOXYGENATING PROCESS AND PRODUCT

Don Scott, Chicago, Ill., assignor to Ben L. Saret, Chicago, Ill.

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This invention relates to a deoxygenating process and product and has particular reference to means for removal of uncombined oxygen from the interior of hermetically-sealed packages or containers.

As is well known, free, uncombined oxygen has a deleterious action on certain products and more particularly on certain food products. Thus in the packaging of such products, it has been the usual practice to remove the oxygen from the package by evacuation and/or nitrogen flushing prior to sealing. Such processes in commercial practice, however, require expensive machinery and the uncombined oxygen is not always completely removed even after successive evacuations and flushings. Accordingly, an object of this invention is to provide means for removing uncombined oxygen from the interior of a hermetically-sealed container after the container has been sealed.

A further object of this invention is the provision of a method for packaging dry products substantially free of gaseous oxygen.

A still further object of this invention is to provide a hermetically-sealed article of manufacture from which substantially all of the uncombined gaseous oxygen has been removed.

A still further object of this invention is the provision of a container or a component part thereof which is particularly suitable for removing uncombined oxygen from the interior of the container after it has been hermetically sealed.

A still further object of this invention is the provision of a deoxygenating capsule which is particularly suitable for removing oxygen from the interior of hermetically-sealed containers or packages.

Further and additional objects will appear from the following description and the accompanying drawing and the appended claims.

In accordance with the disclosure in Dwight L. Baker United States Reissue Pat. No. 23,523, there has been devised an enzymatic process of removing free oxygen from food and other products. In one aspect the procedure described in that patent involves the use of an enzyme system having glucose-oxidase and catalase activities. Thus in accordance with the disclosure in that patent, a food or other product containing water and glucose is stabilized against oxidative deterioration by adding to the product catalase and glucose oxidase. The enzyme system catalyzes the reaction between free oxygen and glucose to produce gluconic acid whereby the oxygen that may be contained within a hermetically-sealed package is substantially completely exhausted therefrom provided that an equivalent or excess amount of glucose is present. As will be apparent from the disclosure in Reissue Patent No. 23,523, the important ingredients of the deoxygenating system include water, glucose, glucose oxidase and catalase. However, the process specifically disclosed in the Baker reissue patent is not applicable for deoxygenating a hermetically-sealed product which is essentially free of water, since an aqueous substrate is re-

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quired for the enzymatic reaction to occur. This invention has particular applicability to the packaging of dry food products and other substances which are normally subject to oxidative deterioration. Thus this invention finds applicability in the packaging of dry soup mixes, dry dessert mixes, dry beverage mixes, coffee, coconut, dry egg constituents, dry vegetable and meat products, dry cereals and the like. As will be apparent as the description proceeds, the invention also has applicability in the packaging of materials other than food products which may be normally subject to oxidative deterioration. For example, such chemicals as ferrous sulfate and certain oils, fats, vitamin preparations, vaccines, sera, miscellaneous biologicals or other substances normally reactive with free oxygen may be packaged in accordance with the process of this invention. In addition, this invention finds applicability in the packaging of certain water-containing products where the nature of the product is such that contaminants cannot be tolerated, or, as in the packaging of sauerkraut, the pH or other conditions in the product are unfavorable to the deoxygenating reaction involving the enzymes, glucose oxidase and/or catalase.

In accordance with one embodiment of this invention, a product has been stabilized against oxidative deterioration by packaging the product in a hermetically-sealed container, said container containing in addition to the product, a deoxygenating body which is out of direct contact with the product; said body comprising a dispersion of water, glucose and an enzyme system having glucose oxidase activity. Normally, such packages when sealed, include a gas or air space which is not completely occupied by the product in the package and, in accordance with one embodiment of this invention, there is disposed in this gas or air space the deoxygenating body above referred to which will serve to remove the oxygen from the gas that may be entrapped in the container after the sealing operation. In order to prevent direct contact between the product being packaged and the deoxygenating body, it is preferred to provide a substantially moisture-proof or water-proof barrier between the body and the product, this barrier being of a character which will permit the diffusion of gaseous oxygen therethrough. Such a barrier may be a sheet of a material such as cellophane, wax paper, a resin-treated paper or a sheet of synthetic plastic such as Pliofilm, flexible styrene, polyethylene, cellulose resins, styrene resins, vinyl polymers, or the like. If desired, the deoxygenating body may be affixed or positioned adjacent an inner side wall of the container itself with the barrier sheet serving to keep it out of direct contact with the product. However, if desired, the deoxygenating body may be enclosed within an envelope formed of the barrier and the resulting capsule may be inserted within the container along with the product prior to sealing the package. An important consideration is, of course, that the oxygen contained within the gas space of the hermetically-sealed container be diffusible through the barrier in such a manner as to be eliminated from the container by virtue of the glucose oxidation reaction.

It is further preferred that the deoxygenating body comprising the glucose and the aqueous enzyme dispersion also contain thickeners, a preservative and a buffer. The thickeners may comprise such substances as agar, gelatine, algin, gums, carboxymethyl cellulose, methyl cellulose, pectin, or an inorganic material such as silica gel and the like. These thickeners are of use in fixing the form and the position of the deoxygenating body within the sealed container and assist in inhibiting the diffusion of moisture through the barrier to the product being packaged, thereby being particularly useful where excess moisture in the packaged product is undesirable. The thickeners may be used in an amount only to in-

crease the viscosity, or may be used in increased amounts to form an actual gel, if desired. Suitable preservatives for the deoxygenating body are dehydroacetic acid, merthiolate or any other substances which will stabilize the body against decomposition by microorganisms and will not inactivate the enzyme system. If a high concentration of glucose is employed in the deoxygenating body, it may not be necessary to utilize a preservative, since such high concentrations will normally have a preservative effect. A buffer such as an alkali metal phosphate, calcium carbonate, sodium acetate and the like is desired to neutralize the gluconic acid formed during the reaction. In this respect, sufficient buffer is added to prevent the pH of the deoxygenating body from falling below about 3 or 4 due to gluconic acid formation since the activity of the enzyme system may be adversely affected under such acid conditions.

In carrying out this invention in one form, a deoxygenating body is prepared by dispersing an enzyme system containing glucose oxidase and catalase in a phosphate buffered, aqueous solution containing glucose, dehydroacetic acid and agar. The resulting dispersion contains 35% glucose, 0.4% dehydroacetic acid, 1.5% agar, 100 Sarett units per milliliter of glucose oxidase and 25 Sarett units per milliliter of catalase. The dispersion is also 0.1 M with respect to sodium acid phosphate and the pH is adjusted to 6.0. A small quantity of this dispersion which is in the form of a gel is then sealed in a suitable envelope of a barrier material such as a sheet of moisture-proof cellophane or is affixed to the inner side wall of a container to be hermetically sealed. The enzyme glucose oxidase and catalase may be prepared in accordance with the procedure outlined in said Reissue Pat. No. 23,523 and the units of glucose oxidase and catalase referred to herein as Sarett units are essentially defined in Dwight L. Baker, United States Patent No. 2,651,592, issued September 8, 1953.

In order to demonstrate the manner in which the deoxygenating body may be used in practice in accordance with this invention, reference will now be made to the accompanying drawing wherein:

Figure 1 is a sectional view of a container embodying the principles of this invention.

Fig. 2 is a fragmentary sectional view illustrating another embodiment of this invention.

Fig. 3 is a perspective view of an encapsulated deoxygenating body prepared in accordance with one embodiment of this invention and utilized in the modifications shown in Figs. 2 and 5.

Fig. 4 is a sectional view of the encapsulated body shown in Fig. 3.

Fig. 5 is a sectional view illustrating another embodiment; and

Fig. 6 is a sectional view illustrating still another embodiment.

With particular reference to Fig. 1, there is shown a package comprising a hermetically-sealed jar 10 containing a dry food product 11 such as a dehydrated soup mix, a powdered dessert mix, powdered egg constituents, or the like, which may normally be subject to oxidative deterioration. Within the container is also an air space 12 positioned above the normal level of the product contained therein, it being understood that the air space also extends below the level of the product into those areas between the solid particles. The jar 10 is hermetically sealed with a metal cap 14 in any desired manner utilizing sealing compounds or gaskets (not shown) for this purpose, if desired. The cap 14 also includes a liner 16 which comprises a sheet of wax paper, resin-impregnated paper, cellophane or like material which is normally water or moisture-proof but is permeable to oxygen gas. The liner 16 may be secured around its peripheral edges to the top of the cover or lid 14. As shown, there is disposed between the liner 16 and the top of the cap 14 a deoxygenating body

18 which, as above indicated, comprises water, glucose and a nonviable enzyme system having glucose oxidase and catalase activities, and may have the specific composition previously mentioned.

After the product 11 has been placed within the jar 10, the cap 14 is applied in the usual manner to provide a hermetic seal. The air or other gas entrapped within the container upon sealing contains gaseous oxygen and this gas is in the air space 12 which extends to the areas between the particles of the food product. After the cap has been applied as above indicated, the oxygen and perhaps other gases will permeate the liner or barrier 16 and the oxygen will react with the glucose to form gluconic acid as is known. Thus a short time after the container has been hermetically sealed, the oxygen will be completely removed from the interior of the package, thereby preventing any oxidative deterioration of the food product 11.

With reference to the modification shown in Figs. 2, 3 and 4, a deoxygenating body 20 having the composition referred to above is sealed within a moisture-proof cellophane tube or envelope 22 by heat sealing at the ends 24, as will be understood. The cellophane 22 is permeable to oxygen and is essentially moisture or water-proof. As shown in Fig. 2, this capsule may be positioned within a double shell closure 26 for a jar 27, said closure comprising an outer shell 28 and an inner shell 30 which are secured together by a peripheral bead 32 or by screw threads as is well known in the closure art. The inner shell 30 is provided with perforations 34 to permit the free passage of gas into the space between the shells containing the capsule. After this package has been hermetically sealed by screwing down the cap 26, the gaseous oxygen is removed from the interior of the package by diffusion into the space between the shells and through the cellophane barrier 22 wherein, by virtue of the enzymes, it reacts with the glucose in the deoxygenating body to form gluconic acid.

Figs. 5 and 6 show modifications in which this invention has been applied to the hermetic sealing of products within metal containers. In Fig. 5 a capsule of the type shown in Fig. 3 is employed and this capsule is merely inserted into the container along with the food product prior to the sealing step and the capsule is in direct contact with the food product 36. However, the deoxygenating body contained within the capsule is out of direct contact with the food product because of the cellophane barrier 22. In Fig. 6 the deoxygenating body 37 is positioned adjacent the top 38 of the can 40 and is held in place by sealing the peripheral edges of a barrier 42 to the top of the can. Thus when the top of the can is removed prior to emptying the product, the deoxygenating body and barrier are removed with the can lid.

It will be apparent from the foregoing description that many other container and package structures may be devised for retaining the deoxygenating body out of direct contact with the product which is to be hermetically sealed within the container. An important consideration is to provide an oxygen gas permeable barrier for keeping the deoxygenating body out of direct contact with the product that is sealed in the container.

It will be apparent that the size of the deoxygenating body and the concentration of the various ingredients therein may be widely varied without departing from the spirit and scope of this invention and will be dependent in part upon the amount of oxygen that must be removed from the hermetically-sealed package and the rapidity of removal which is desired. Larger sizes and increased concentrations of glucose oxidase will generally favor the removal of larger amounts of oxygen at more rapid rates. For example, 1/4 ounce (approximately 7 grams) of a deoxygenating body having the approximate composition and enzyme activities of the specific example given above will contain about 700 Sarett units of glucose oxidase and

about 175 units of catalase, together with a large excess of glucose. Assuming that the diffusion of oxygen through the barrier is not a limiting factor, this body has a capacity of taking up about 5 milliliters of oxygen per minute at room temperatures. Thus a deoxygenating body of this size and composition has the potential of removing the oxygen from about ½ pint of air in a matter of minutes. In applications where comparatively large volumes of oxygen are to be removed, the deoxygenating body should be heavily buffered, as for example with calcium carbonate, to prevent a pH drop which will impair or stop the enzymatic reaction. Thus about ½ gram of gluconic acid is formed in removing 50 milliliters of oxygen from a gas and the use of about one gram of calcium carbonate in the deoxygenating body would be sufficient to effectively neutralize the gluconic acid formed. The carbon dioxide thus produced will diffuse back through the barrier, thereby preventing the accumulation of gas under pressure in the side of the barrier next to the deoxygenating body. If only a small amount of oxygen, say 2 milliliters, is to be removed from a container, a deoxygenating body having a volume of 2 milliliters with a glucose oxidase activity of one Sarett unit per milliliter will remove the oxygen in a matter of an hour or so. Generally speaking, in practical applications, the concentration of glucose oxidase in the deoxygenating body should be in excess of about one Sarett unit per milliliter, while the catalase (if present at all) need be present only in traces but suitably in excess of about 0.1 Sarett unit per milliliter. Also, the total amount of glucose present must be at least equal to the stoichiometric equivalent of the amount of oxygen gas to be removed from the sealed container.

In the foregoing example, the deoxygenating body has been referred to as one which contains catalase in addition to glucose oxidase. As pointed out in Baker Reissue Patent No. 23,523, a function of the catalase is to destroy the hydrogen peroxide formed by the glucose oxidase reaction which destruction is desirable to prevent the accumulation of hydrogen peroxide directly in the packaged product, since hydrogen peroxide may be more deleterious than oxygen itself. However, in accordance with this invention the accumulation of the hydrogen peroxide in the deoxygenating body is not so objectionable and accordingly it is permissible to permit its accumulation therein. Thus, in its broader aspects, catalase may be eliminated from the deoxygenating body and the oxidation reaction is allowed to occur with the accumulation of hydrogen peroxide which, because of the barrier, remains out of direct contact with the hermetically sealed product which is to be preserved against oxidative deterioration.

Also, in accordance with this invention, glucose oxidase and a glucose substrate have been referred to as being important ingredients of the deoxygenating body. However, other oxidases or dehydrogenases that are capable of catalyzing a reaction between molecular oxygen and a specific substrate for the particular oxidase or dehydrogenase in an aqueous medium may also be employed. Thus, as pointed out in said Reissue Patent No. 23,523, molecular oxygen will combine with (1) phenols and catechols in the presence of tyrosinase, (2) aldehydes and purines in the presence of aldehyde oxidase, (3) amino acids in the presence of amino acid oxidase, (4) uric acid in the presence of uricase, (5) mannose or galactose in the presence of mannose oxidase or galactose oxidase, (6) monoamines and diamines in the presence of amine oxidase, (7) unsaturated fatty acids in the presence of lipoxidase, and (8) vitamin C in the presence of ascorbic oxidase. An important consideration is that the deoxygenating body containing the enzyme and its substrate in aqueous dispersion be out of contact with the product in the package and preferably be separated therefrom by a substantially moisture-proof gas-permeable barrier.

It will be seen that means has been provided for remov-

ing uncombined oxygen from the interior of hermetically-sealed containers by utilizing a deoxygenating body which is out of direct contact with the packaged product. The invention is particularly useful in the packaging of essentially dry products. The term "dry products" used herein is not intended to be restricted to anhydrous products but is intended to mean commercially dry or dehydrated products which may be used to designate powdered, granulated, granular or concentrated materials, as well as materials containing liquids other than water, such as oils or organic solvents or dispersants.

By use of this invention, no special means are required to evacuate or flush air from the package prior to sealing. The container is sealed with entrapped air and the oxygen is gradually removed from such air by absorption into the deoxygenating body. Care should be exercised not to expose the deoxygenating body to atmospheric oxygen for extended periods prior to sealing the container since it may thereby be rendered ineffective for the intended purposes, as will be understood. This invention also finds application in the successive removal of oxygen from containers having closures which are periodically removed and reapplied, since upon reapplication, the entrapped oxygen will again be removed as before. In those instances, the deoxygenating body may be replaced if its capacity to take up oxygen has become impaired or is exhausted. This is a feature of the structures particularly shown in Figs. 2 and 5 of the drawings.

While particular embodiments of this invention are shown above, it will be understood, of course, that the invention is not to be limited thereto, since many modifications may be made, and it is contemplated, therefore, by the appended claims to cover any such modifications as fall within the true spirit and scope of this invention.

I claim:

1. An article of manufacture comprising a hermetically-sealed package containing a product normally subject to oxidative deterioration, a deoxygenating body, and a moisture proof oxygen-permeable barrier interposed between said product and said body to prevent direct contact therebetween, said body comprising a dispersion of water, glucose and an enzyme system having glucose oxidase activity.

2. An article of manufacture comprising a hermetically-sealed package containing an oxygen depleted gas space, a product normally subject to oxidative deterioration, a deoxygenating body in said gas space out of direct contact with said product, and a substantially moisture-proof oxygen-permeable barrier between said product and said body, said body comprising a dispersion of water, glucose and a nonviable enzyme system having glucose oxidase and catalase activities.

3. An article of manufacture comprising a hermetically-sealed package containing an oxygen-depleted gas space, a dry food product normally subject to oxidative deterioration, and a capsule in said gas space, said capsule comprising a substantially moisture-proof oxygen-permeable sheath enclosing a body of a dispersion of water, glucose and a nonviable enzyme system having glucose oxidase and catalase activities.

4. An article of manufacture comprising a hermetically-sealed package containing an oxygen-depleted gas space, a dry food product normally subject to oxidative deterioration, a deoxygenating body in said gas space positioned adjacent an inner side wall of said package, and an oxygen-permeable moisture-proof barrier between said product and said body to prevent direct contact therebetween, said body comprising a dispersion of water, glucose and an enzyme system having glucose oxidase and catalase activity.

5. The article recited in claim 1 wherein said body also includes a buffer.

6. The article recited in claim 3 wherein said body also includes a thickening agent and a buffer.

7. The article recited in claim 4 wherein said body

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also includes a thickening agent, a preservative and a buffer.

8. A process of packaging a product normally subject to oxidative deterioration which comprises introducing said product into a hermetically-sealable container, positioning within said container a deoxygenating body shielded from direct contact with said product by a substantially waterproof oxygen-permeable sheet, said body comprising a dispersion of water, glucose and an enzyme system having glucose oxidase activity, and hermetically sealing said container to entrap an oxygen-containing gas therein in contact with said product and said sheet whereby after sealing the oxygen in said gas is eliminated by diffusion through said sheet and reaction with the glucose in said body.

9. A process of packaging a dry food product normally subject to oxidative deterioration which comprises introducing said product into a hermetically-sealable container, positioning within said container a deoxygenating body shielded from direct contact with said product by

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a substantially waterproof, oxygen-permeable sheet, said body comprising a dispersion of water, glucose and a nonviable enzyme system having glucose oxidase and catalase activities, and hermetically sealing said container to entrap an oxygen-containing gas therein in contact with said product and said sheet whereby after sealing the oxygen in said gas is eliminated by diffusion through said sheet and reaction with the glucose in said body.

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