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W. P. CASEY, JR., ET AL

3,712,848

DEOXYGENATED PACKAGE

Original Filed Feb. 6, 1964

Fig. 1

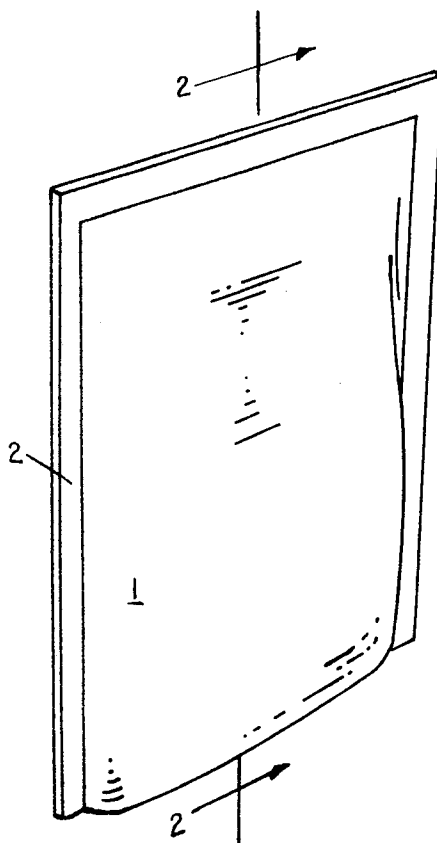
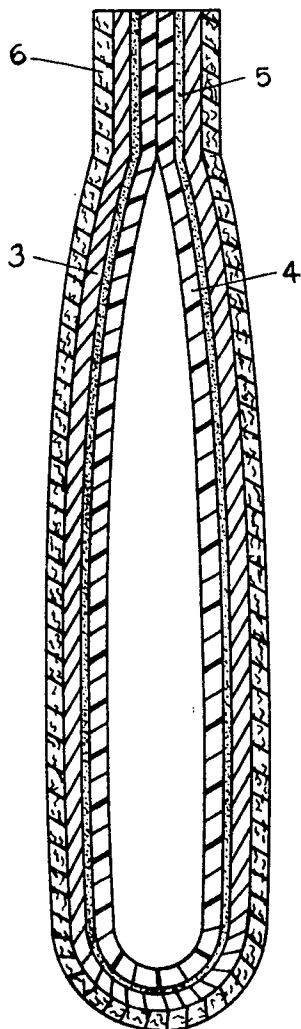


Fig. 2

INVENTORS
WILLIAM P. CASEY, JR.
FRANK G. GRUNDMAN
BY *Allen O. Maki*
Coy S. Verhaegh
ATTORNEYS

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DEOXYGENATED PACKAGE

William P. Casey, Jr., and Frank G. Grundman, Neenah, Wis., assignors to American Can Company, New York, N.Y.

Continuation of application Ser. No. 343,622, Feb. 6, 1964. This application Sept. 4, 1969, Ser. No. 856,899

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U.S. Cl. 161—213

1 Claim

ABSTRACT OF THE DISCLOSURE

A laminar sheet material including a gas and water impermeable layer, a gas permeable and water impermeable layer and a bonding material therebetween containing a catalyst capable of initiating reaction between hydrogen and oxygen to form water. In a sealed pouch formed of the sheet, oxygen is removed by formation of water which is trapped between the two layers and thus out of contact with the packaged product.

This application is a continuation of application Ser. No. 343,622, filed Feb. 6, 1964 and now abandoned.

This invention relates to deoxygenated packages for storing substances such as foods normally subject to oxidative deterioration and to sheet materials from which such packages may be formed.

In the past, various attempts have been made to devise means for removing oxygen from a package by the use of in-package oxygen removers. Hitherto such packages have not enjoyed large scale commercial success because of the various shortcomings thereof. The systems most commonly used at present rely on the use of moisture-containing oxygen removers, such as enzymes having glucose oxidase and catalase activity. These systems are difficult to ship and store since they use up their oxygen removing capacity if permitted to be exposed to the atmosphere for extended periods of time. Other attempts have been made to place inorganic oxidation reduction (redox) catalysts inside of packages into which hydrogen is introduced in order to remove the oxygen by reaction with such hydrogen. However, such catalysts have been either in contact with a food product such as dried milk contained in the package or placed in the package in a separate capsule or in the form of pellets. Such capsules or pellets present a distasteful appearance in a food product and also constitute a possible hazard to the consumer who might inadvertently eat them. In addition, insertion of capsules or pellets complicates the filling operation performed by the packager. Particular difficulties have been encountered in attempts to package and store dried whole milk. Moisture-containing oxygen removers are unsatisfactory because any moisture contained therein will deteriorate the powdered milk. Also the expense involved in storing this product in a hermetically sealed rigid metal container is too great to render such methods practical. Insertion of inorganic oxidation catalysts into the packaged product gives the appearance of distasteful contamination.

The present invention overcomes these difficulties by providing a sheet material which may be shipped and stored without special precautions and which has dry redox catalyst within the sheet material which catalyst is not exposed to the contents of a container formed from the sheet material.

The present invention for the first time makes possible the packaging of whole dried milk powder in a flexible pouch or envelope at a low cost without the use of any oxygen removing capsule or pellet within the package and yet maintains the powdered milk under suitable conditions to prevent deterioration.

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A preferred embodiment of the invention is shown in the drawings in which:

FIG. 1 is a perspective view of a pouch formed in accordance with the present invention, and

FIG. 2 is a cross-sectional view of the pouch of FIG. 1 along line 2—2 with the cross section of the pouch material magnified to show the structure of the same.

With particular reference to FIG. 1, there is shown a package comprising a hermetically sealed pouch 1 containing a food product such as dried whole milk. Pouch 1 is shown as being sealed along three edges as for example at 2, but any other conventional pouch configuration could be used instead.

As seen in FIG. 2, the pouch of the present invention is formed from a sheet material having a plurality of layers. The layers which are essential to the package are a gas and water impermeable barrier layer 3, preferably composed of metal foil and an inner layer 4 formed of a water impermeable but gas permeable material. The catalyst is disposed at 5 between these two layers and thus is in contact with the gas phase of the interior of the package and yet is separated from any solid or liquid product contained therein.

Material 4 is shown in FIG. 2 to be a resinous plastic material such as polyethylene but this layer may be formed from any equivalent material for example polypropylene or various other suitable polyolefins, cellophane, polyvinyl chloride, rubber hydrochloride, or wax-copolymer blends, such as blends of wax and ethylene-vinyl acetate copolymers.

It is preferred to disperse the catalyst in an adhesion promoting material 5 as shown in FIG. 2, but if desired the catalyst may merely be applied between layers 3 and 4 before the lamination by sprinkling, brushing, spraying or by depositing electrolytically, electrostatically or from a metal-containing vapor. In practice, layer 5 is usually very thin, often little more than a monomolecular layer. Examples of adhesion promoting materials which may be used to assist the adhesion of polyolefin resins applied to metal foil are polyethylene imine, titanium acetyl acetate, and shellac. It is preferred to apply these adhesion promoters, commonly referred to as "anchor coats," or "primers" from a solution in a liquid such as isopropyl alcohol. Another type of adhesion promoting material which may be used is vinyl chloride, which may be applied in a form of a solution in either toluene, methyl ethyl ketone, alcohols or combinations thereof. Such a coating is commonly applied to metal foil to protect the foil and to promote the adhesion thereto of hot-melt coatings such as wax-copolymer blends. Obviously layer 5 could as well be an adhesive or glue which could be employed to laminate layers 3 and 4. If the catalyst is mixed within the adhesion promoting material, this material itself should be gas permeable in order that the catalyst be accessible to the gas phase of the contents of the container. If the adhesion promoting material is not gas permeable, the catalyst could be sprinkled on the surface of layer 5 thereby placing the same in contact with the undersurface of the permeable layer 4. The catalyst may thus be incorporated into any adhesion promoting material—in an anchor coat in the case of extrusion coating, in a protective coat in the case of a hot-melt coating, or in an adhesive used to bond the two layers together. "Adhesion promoter" is defined to include all of these for purposes of the subject specification and claims. As shown in FIG. 2 a further layer 6 of a decorated material such as paper may be placed around the outside of the package for purposes of applying trade names and also to protect the gas impermeable barrier layer against abrasion or the like. While impermeable layer 3 is shown as being com-

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posed of metal, it is to be understood that other substantially impermeable materials may be substituted, for example, polyvinylidene chloride.

The preferred composition of the catalyst is palladium either in finely divided form such as palladium black or in the form of a thin coating on a carrier such as finely divided alumina. Palladium is preferred as the redox catalyst for economic reasons, but it will be obvious to those skilled in the art that equivalent substances such as the other platinum group metals or organic tin compounds can be substituted therefor.

In forming packages in accordance with the present invention, the product is placed within the pouch and the oxygen is removed from the interior of the same to that extent which is possible by direct flushing with an inert gas, in the present case preferably containing at least 5% hydrogen, or by creating a vacuum within the package and thereafter introducing a gas which contains hydrogen. The pouch is then sealed and is ready for placement within a carton, if desired, for shipment and storage. These conventional methods of vacuum packaging, flushing with an inert gas or combinations of these methods leave a residual amount of approximately 1-2% oxygen in the gas phase of the container and this residual amount should be removed in order to adequately protect the dry food powder. The residual oxygen is essentially removed from the package over a period of time due to combination with the hydrogen gas present. Oxygen desorbed from the product packaged is also removed by this system, as is oxygen which enters the package through areas of low level transmission. The small amount of water formed from this reaction is believed to be formed in the vicinity of the catalyst between layers 3 and 4. Thus the dry food powder is shielded by layer 4 from any moisture produced by the oxidation reaction.

The present invention is illustrated further by the following examples but is not limited thereto.

EXAMPLE I

Stock material was prepared by laminating 30 lb./ream paper and 0.00035 inch aluminum foil, polyethylene being extrusion coated onto the foil to serve as medium for bonding these layers together. A polyethylene imine anchor coat was applied to the other side of the film as a 0.25 percent solution in isopropanol. 4 lb. of this solution was applied to each ream of material and the solvent subsequently removed by evaporation. This polyethylene imine solution also contained enough finely divided palladium to provide 0.005 lb./ream. A layer of polyethylene 1½ mils thick was extruded over this catalyst-containing anchor coat. Similar stock material was made with the catalyst omitted for purposes of comparison. A number of pouches were formed from both of these stock materials, and four freeze dried shrimp were placed in each pouch. The pouches were flushed with a gas containing 5% H₂ and 95% N₂ and analyzed for oxygen content immediately after sealing and at intervals thereafter. The results of these tests are summarized in Tables I and II.

TABLE I

Pouches Containing Shrimp With No Catalyst			
Pouch No.	Oxygen content, percent		
	t=0 hrs.	t=48 hrs.	t=7 days
1-----	0.30	0.30	0.30
2-----	0.57	0.57	0.57
3-----	0.33	0.34	0.36

TABLE II

Pouch Containing Shrimp With Catalyst			
Pouch No.	Oxygen content, percent		
	t=0 hrs.	t=48 hrs.	t=7 days
4-----	1.13	0.87	0.18
5-----	0.70	0.50	0.01
6-----	0.81	0.50	0.02

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EXAMPLE II

Pouches containing dried whole milk, known to desorb significant amounts of oxygen, were formed from both of the stock materials prepared in Example I. Each pouch was again flushed with a gas containing 95% N₂ and 5% H₂ and sealed. The oxygen contents at various times are listed in Table III and IV:

TABLE III

Pouches Containing Dried Whole Milk With No Catalyst

Pouch No.	Oxygen content, percent		
	t=0 hrs.	t=48 hrs.	t=7 days
7-----	1.44	1.86	1.90
8-----	1.27	1.75	1.81
9-----	1.91	2.49	2.56

TABLE IV

Pouches Containing Dried Whole Milk With Catalyst

Pouch No.	Oxygen content, percent		
	t=0 hrs.	t=48 hrs.	t=7 days
10-----	1.25	1.31	0.68
11-----	1.03	0.93	0.53
12-----	1.51	1.38	0.88

While particular embodiments of this invention have been described herein, it will of course be understood the invention is not limited thereto since various modifications will readily be apparent to those skilled in the art. Therefore it is contemplated that the invention shall be limited only by the scope of the appended claim.

We claim:

1. A laminated, flexible, sheet material adapted to be formed into a gas impervious container, comprising:

- a first flexible sheet material layer, said first layer being substantially impervious to oxygen and water vapor and chosen from the group consisting of flexible metal foil and polyvinylidene chloride film;
- a second flexible sheet material layer, said second layer being substantially pervious to oxygen and hydrogen and being substantially impervious to water and chosen from the group consisting of polyethylene, polypropylene, cellophane, polyvinyl chloride and rubber hydrochloride; and
- a third, bonding layer, said third layer being a gas-permeable, adhesion-promoting material entirely disposed between and bonding together said first and second layers, and including, substantially evenly distributed in said third layer, a finely divided catalyst chosen from the group consisting of the platinum metals and adapted to convert oxygen and hydrogen to which said second layer is pervious into water to which said second layer is impervious, whereby any water so formed is effectively trapped between said first and second layers.

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WILLIAM J. VAN BALEN, Primary Examiner
R. J. ROCHE, Assistant Examiner

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161—216, 218, 254; 99—171, 189; 229—3.5