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SYSTEM FOR PACKAGING

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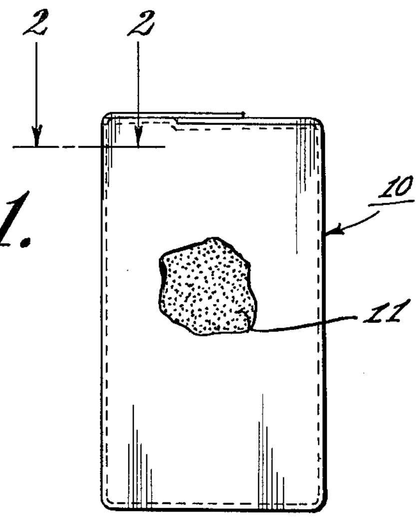

Fig.1.

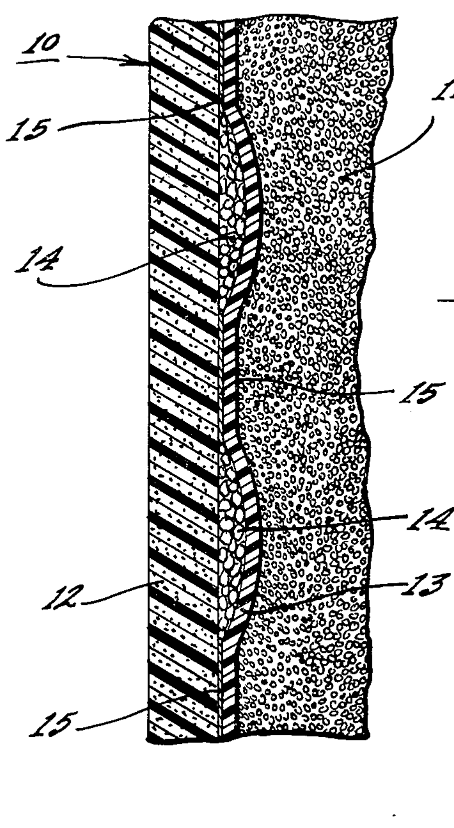

Fig.2.

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SYSTEM FOR PACKAGING

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This invention relates to a system for packaging goods which are desirably stored under non-oxidizing conditions. Heretofore there have been systems in which an inert gas was included in a package containing goods sensitive to the presence of oxygen. As explained in British Patent 734,197, a water synthesis catalyst can be included in a package containing an inert gas and a minor amount of hydrogen adapted to react with the trace amounts of oxygen for enhancing the preservation effectiveness of the inert gas. Rosenblatt 2,582,885 describes one form of water synthesis catalyst adapted to remove trace amounts of oxygen from technical grades of nitrogen by combustion of the hydrogen introduced for such purification. Lindewald 2,789,059 describes one system whereby an inert gas in a warehouse may be maintained by circulating a mixture of inert gas and hydrogen through a catalytic zone for water synthesis.

In accordance with the present invention, particles of water synthesis catalyst having a particle size within the range from about 1 millimicron to about 500 microns are positioned between a plastic sheet functioning as gas permeable membrane exposed to the internal portion of the package and a gas impermeable sheet such as aluminum foil or glycol terephthalate film. The gas permeable plastic sheet serves to protect the goods from contact with the catalyst. Such shielded, finely divided particles of water synthesis catalyst remove trace amounts of oxygen from the packaging gas of the present invention which packaging gas is a mixture consisting of from about 95% to about 97% cryogenically purified nitrogen and not less than 3% nor more than 5% hydrogen by volume. By the present invention, the danger of accidental fire during the filling or opening of the package is eliminated notwithstanding the well-known flammability of mixtures of air and hydrogen.

When a package containing a mixture of nitrogen and hydrogen is opened, the hydrogen gas and the catalyst for synthesizing water are exposed to atmospheric oxygen. If the quantity of hydrogen in the nitrogen-hydrogen mixture is excessive, a fire and/or explosion hazard could result from the exposure of air and hydrogen to the water synthesis catalyst. An important advantage of the gas mixture of the present invention is the non-flammability of the gas mixture resulting from mixtures of air with 95% nitrogen, 5% hydrogen in any proportion.

The establishment of 5% as the maximum hydrogen content permissible without encountering a flammability hazard helps to transform hydrogen as a packaging gas from a frightening theory to a commercially attractive practice. The well-known explosion hazards connected with the use of gaseous hydrogen in factories has tended to prompt managers of plants packaging food under inert gas to dismiss the proposal of using hydrogen as merely of theoretical interest. However, the assurance of the non-flammability of plausible mixtures of air and the hydrogen containing inert gas of the present invention overcomes this otherwise insurmountable obstacle.

By a series of tests it is established that if the hydrogen concentration is insufficient, the probability of prompt conversion of oxygen to water is significantly reduced. Although only two volumes of hydrogen per volume of

oxygen are theoretically necessary, reliable minimizing of the oxygen content of the inert gas requires a hydrogen to oxygen ratio of at least 3 to 1 in accordance with the present invention. Because some goods preferentially sorb relatively large amounts of oxygen, and because the volume of inert gas ordinarily employed in consumer packages is relatively small, the 3 to 1 minimum ratio of hydrogen to conceivable maximum oxygen concentration sometimes necessitates the redesign of the package to provide a larger volume of inert gas than was previously conventional. Any massive puncturing of the sealing of the package destroys the storage stability of the package, but the 3 to 1 ratio requirement and 5% hydrogen permits tiny leaks of air into the inert gas over a prolonged period without permitting the goods to undergo oxidative degeneration. Hydrogen tends to leak preferentially from any such tiny leaks, so the probabilities of successful preservation are enhanced by the use of a gas mixture containing the preferred 5% hydrogen instead of a lower concentration.

Particular attention is directed to the feature of employing cryogenically purified nitrogen. In some previous inert gas systems, carbon dioxide has been employed either alone or as a component of a gas consisting predominantly of nitrogen and derived from flue gas. In the development of the present invention, the surprising discovery was made that trace components in such modified flue gas tend to impair the usefulness of a system for storage of foods, seeds, tobacco, etc., and that greater reliability of retention of flavor and other difficulty measured properties was achieved using cryogenically purified nitrogen as the inert gas. In archives, and/or warehouses employing inert gas merely for fire protection, nitrogen derived from flue gas might be cheaper and hence the preferred inert gas for admixture with a minor amount of hydrogen for circulation through a water synthesis catalyst. However, in accordance with the present invention, cryogenically purified nitrogen is employed (in admixture with from about 3% to 5% by volume hydrogen) as the inert gas in a package containing water synthesis catalyst which is finely divided and shielded by a permeable plastic film and such feature enhances the reliability of the packaging for features such as flavor retention. Just what are the trace components present in inert gas derived by purification of flue gas but absent from cryogenically purified nitrogen is not known, but carbon dioxide is deemed more likely troublesome than bacteria, dust, moisture, or related contaminants. Cryogenically purified nitrogen is only a technical grade, and contains whatever amounts of argon, helium, etc., are not profitably salvaged during the production of nitrogen. A significant portion of the cryogenically purified nitrogen is routinely processed over a water synthesis catalyst to lower the oxygen concentration to less than 1 p.p.m., but because the present invention employs a water synthesis catalyst, the inert gas can include the trace amounts of oxygen resulting from commercial nitrogen production.

The nature of the invention is further clarified by reference to the accompanying drawings. In the drawings, FIGURE 1 schematically shows a plastic bag **10** containing goods **11** (e.g., powdered milk) and a gas mixture consisting essentially of cryogenically purified nitrogen and about 4% hydrogen. FIGURE 2 is a cross-section taken along line **2—2** of FIG. 1 of a segment of the thickness of the bag **10**, and shows an outer sheet of a gas impermeable material **12**, a gas permeable sheet **13** at the inside of the package, and finely divided particles of water synthesis catalyst **14** interposed therebetween. At at least some zones, the inner sheet **13** is bonded to the outer sheet **12** at bonding zones **15**.

Examples of sheet materials suitable as the gas impermeable sheet **12** include aluminum foil, plastic laminates having aluminum cores, and 10 mil films of glycol terephthalate. Examples of gas permeable film **13** include 2 mil polyethylene, thin polyvinylalcohol and thin polyvinylacetate. The catalyst particles **14** can be secured to at least one of the two sheet materials of a flexible package by means of an adhesive such as varnish or by mechanical means.

It is often desirable to secure the catalyst particles to a sheet material by employing the catalyst particles as the thickener for an ink printed onto a sheet material. If desired, the sorptive carrier particles may be adhered to one of the films prior to the impregnation of the solution of the compound of the noble metal functioning as the water synthesis catalyst into the sorptive carrier. As shown in the drawing, a somewhat quilted structure may be provided so that the catalyst particles are secured to zones spaced from each other, whereby portions of the bonding zones **15** securing the gas permeable film to the opposing face of the sandwich are at spaced locations. If desired, the catalyst particles **14** can be printed uniformly onto the permeable film **13** which can be adhered to the nonpermeable sheet **12** without any planned unbonded areas. The readiness with which the hydrogen and oxygen diffuse through a thin permeable plastic film is so great that only a few mills (tenths of a cent) worth of catalyst can suffice even when the catalyst particles are embedded between the lamina of the sandwich. Even lower catalyst costs are generally achieved by the spaced lines of bonding zones **15** of the quilted structure shown schematically in FIGURE 2. If desired, the catalyst particles **14** and permeable sheet **13** can be positioned merely near the top of the bag adjacent to the normal location of the hydrogen-containing-nitrogen.

The invention may be further clarified by reference to the following example:

EXAMPLE I

A small package of powdered milk comprises a bag formed from aluminum foil. Particular attention is directed to the gas permeable sheet of polyethylene bonded in quilt-like fashion to the aluminum foil, thus defining a plurality of small compartments spaced from each other. In each compartment, a small amount of finely pulverized water synthesis catalyst consisting of 0.1% palladium on sorptive alumina is positioned in such a way as to be effective as a water synthesis catalyst. The sorptive eta alumina particles are prepared by dehydration of high purity beta alumina trihydrate. Eta alumina particles within the size range from 200 microns to 400 microns are partially embedded into heat-softened film of 2 mil polyethylene. The thus adhered particles are spaced zones of a checkerboard embossed film. The particle are impregnated with an aqueous solution of chloropalladic acid, dried under vacuum, and treated with hydrogen. The polyethylene sheet having the adhered particles of palladium on eta alumina is adhered to the alunminum foil at the gridiron pattern lines, and the thus prepared sandwich structure is fabricated into a bag. The bag is filled with the mixture of 95% cryogenically purified nitrogen and 5% hydrogen, and advanced through a filling machine in which powdered milk displaces most of the gas, and the package is sealed. After storage for several months, tests on randomly selected packages establish the absence of oxygen and the presence of hydrogen in the gas in the package. Moreover, the flavor retention for the powdered milk is excellent for such prolonged storage.

EXAMPLE II

An apparatus is set up for evaluating gas permeable membranes and/or water synthesis catalysts. A gas stream flows through the test chamber, through a constant temperature zone, and then through an oxygen detection zone comprising a bed of eta alumina pellets impregnated with about 5% palladium, and equipped with thermocouples for detecting any temperature increase. By a series of tests it is shown that each of palladium and platinum catalyze at ambient temperatures the flamless reaction of 0.5% oxygen in a gas mixture comprising about 4.5% hydrogen and 95% nitrogen, but that certain other oxidation catalysts are effective only at higher temperatures. At a concentration within the range from about 0.1% to 1%, palladium and/or platinum are effective on a variety of sorptive supports, including alumina and silica. By a series of tests it is established that the particle size must be within the range from 1 millimicron to 500 microns for the reliable catalytic effectiveness for cooperation with flexible film of gas permeable membrane. For example, the weight of a 10 mm. bead of silica impregnated with 0.1% palladium is great enough that during shifting of a package during shipment, the bonding of a gas permeable film to an outer sheet might be broken, whereas the smaller weight of the tiny catalyst particles of the present invention imposes no such strain during the lurching of cargo. Particles too small in size are not readily positioned between the walls of a multi-wall bag. Particles smaller than about 10 microns would ordinarily be less advantageous than particles of the 10–500 micron range, but particles as small as 1 millimicron are deemed to have some suitability as water synthesis catalysts.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

The invention claimed is as follows:

1. A consumer package of food protected from loss of flavor by a packaging gas, said packaging gas being prepared by cryogenically purifying nitrogen, and adding a minor amount of hydrogen thereto to provide a mixture consisting of not less than 3% nor more than 5% hydrogen and from 95% to 97% cryogenically purified nitrogen, said gas being confined in contact with the food by gas impermeable sheet material imparting structural strength to the package; catalyst particles consisting of a sorptive carrier and from 0.1% to 1% noble metal of the group consisting of palladium, platinum and mixtures thereof deposited in said sorptive carrier, said particles having a size range from about 200 to about 400 microns; a thin film of plastic protecting said catalyst particles from contact with the food, said thin film being bonded to the inner surface of the gas impermeable sheet at spaced bonding zones defining small compartments for said catalyst particles, whereby each catalyst particle is maintained within its small compartment even during lurching of the food package during transportation thereof, said thin plastic film permitting the diffusion of oxygen, nitrogen and hydrogen to, from and between the zone adjacent the catalyst particles and the zone adjacent the food, whereby any residual oxygen sorbed on the packaged food diffuses to the catalyst particle for conversion to water vapor.

2. In the method of protecting the flavor of food by packaging the food in a consumer package containing both a water synthesis catalyst and a hydrogen containing gas, the improvement which consists of: employing not less than 3% nor more than 5% hydrogen in the gas sealed in the package; employing a volume ratio of hydrogen to expected oxygen of at least 3 to 1 such oxygen comprising oxygen sorbed on the packaged food; cryogenically purifying nitrogen to provide the inert gas constituting 95 to 97% of the gas sealed in the package; employing particles of water synthesis catalyst within the size range from about 200 to about 400 microns, said catalyst particles consisting of a sorptive carrier and from 0.1% to 1% noble metal of the group consisting of palladium platinum and mixtures thereof deposited in said sorptive carrier; and shielding the water synthesis catalyst particles from the food by positioning such catalyst particles in small compartments defined by the spaced bonding zones securing a thin gas permeable plastic film to the inner surface of the structurally strong sheet of gas impermeable material of said package, whereby each catalyst particle is maintained within its small compartment even during lurching of the food package during transportation thereof, said thin plastic film permitting the diffusion of oxygen, nitrogen and hydrogen to, from and between the zone adjacent the catalyst particles and the zone adjacent the food, whereby any residual oxygen sorbed on the packaged food diffuses to the catalyst particle for conversion to water vapor.

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