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2,765,233

ENZYME-TREATED SHEET PRODUCT AND ARTICLE WRAPPED THEREWITH

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This invention relates to a sheet product and to an article wrapped therewith and has for one object the provision of an enzyme-treated fabric sheet for wrapping a moist food product which is normally subject to oxidative deterioration upon exposure to atmospheric oxygen.

Certain food products such as cheese or butter are normally subject to oxidative deterioration due to exposure to atmospheric oxygen over long periods of storage. These products are normally packaged or wrapped in moistureproof paper in order to prevent spoilage by drying. However, such papers although moistureproof are gas-permeable so that oxygen may penetrate the wrapping, whereby oxidative deterioration of the product may result after periods of prolonged storage. It has been proposed in the past to wrap such articles in gas-impermeable metal foil. However, metal foil is comparatively expensive and it is desirable, where possible, to employ less expensive fabric sheet material, such as moistureproof paper or sheets of the various types of synthetics that are well known to the art. As indicated above, these paper sheets and organic synthetics are usually gas-permeable so that products wrapped in them are not fully protected against oxidative deterioration. Also certain frozen foods, such as sliced peaches, are subject to rapid oxidative deterioration during the step of defrosting prior to use, causing them to turn brown. This particular browning reaction has been attributed to an enzymatic reaction involving the enzyme tyrosinase.

Accordingly, it is a further object of this invention to provide a normally gas-permeable fabric sheet which, when used as a wrapper for a moist article, will protect that article against oxidative deterioration under prolonged storage conditions.

A further object of this invention is the provision of a fabric or paper sheet which is inexpensive to prepare but which will effectively prevent the penetration of oxygen into a moist food product wrapped therewith.

A still further object of this invention is the provision of a fabric or paper sheet which is treated with an enzyme which in the presence of glucose will react with atmospheric oxygen, thereby effectively preventing the penetration of oxygen into a moist food product wrapped or covered therewith.

A still further object of this invention is the provision of a moist solid article, such as a food product, normally subject to oxidative deterioration wrapped or at least partially covered with a gas-permeable fabric sheet having associated therewith an enzyme which in the presence of glucose will substantially prevent the passage of atmospheric oxygen into the wrapped or covered article.

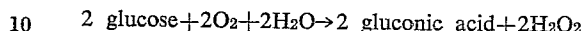
An additional object of this invention is to provide means for protecting a frozen food package, such as sliced peaches, from oxidative browning when the package is thawed prior to consumption.

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

As pointed out in United States Reissue Patent No. 23,523 to Dwight L. Baker, dated July 22, 1952, an

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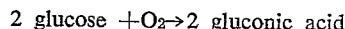
enzyme system comprising glucose oxidase and catalase in the presence of water and glucose is effective for removing oxygen from the interior of a sealed container whereby the material within the container is stabilized against oxidative deterioration. The enzyme glucose oxidase catalyzes the reaction between glucose, oxygen and water to form gluconic acid and hydrogen peroxide in accordance with the following equation:



The catalase effects the decomposition of the hydrogen peroxide as rapidly as it is formed in accordance with the following equation:



Combining the above two equations, it will be noted that the over-all reaction is as follows:



Thus the enzyme system comprising glucose oxidase and catalase in the presence of water will catalyze the reaction between glucose and oxygen to produce gluconic acid which latter is innocuous in food products.

In accordance with the present invention, the principles indicated above have been utilized in connection with the packaging of food products, such as cheese, butter, certain frozen food products or other moist articles, normally wrapped in paper and normally subject to oxidative deterioration upon contact with air. In accordance with one embodiment of this invention, a fabric sheet of paper or other material is provided which is coated or impregnated with an enzyme comprising glucose oxidase and catalase. When such a sheet is used to wrap a moist article which may contain a small amount of glucose, the enzyme system serves as a barrier for the oxygen which would otherwise diffuse through the sheet and into the product since, as the oxygen passes through the sheet, it is at once reacted with the glucose to form innocuous gluconic acid. In the packaging of articles which do not normally contain glucose, the paper or fabric sheet may also be coated or impregnated with glucose along with the enzyme system. Also certain products to be packaged may normally contain catalase. Thus certain types of cheese may contain this substance. In such an event, it would not be necessary to add catalase to the material impregnated into or coated on the wrapping sheet and in that event the wrapping sheet need only contain the enzyme glucose oxidase together with glucose if the latter is not normally present in the product to be wrapped.

In its broad aspects the wrapping or cover sheet of this invention may be impregnated with a solution containing the enzyme system or a moistureproof sheet may be coated with the enzyme system at least on that surface of the sheet which will be in contact with the article being wrapped. If the enzyme system is applied as a coating, it may be applied in conjunction with a suitable binder which is preferably of the water-dispersible type. Thus a suitable binder may be a water-dispersible polyvinyl alcohol, carboxymethyl cellulose, starch, various types of proteins such as casein and the like. The coating or impregnating step may be carried out by any of the techniques that are well known to those skilled in the paper art. However, in the process, care should be taken that the enzyme system in the moist state is not subjected to temperatures in excess of about 70° C. for any substantial period of time since otherwise the enzyme may be inactivated. Likewise the coating or impregnating should be effected in such a manner that the enzymes actually come into contact with the moist product being wrapped adjacent the interface so that the essential ingredients for the two-step oxidation reaction outlined above are all present adjacent the outer surface of the

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wrapped article and preferably at the interface between the article and the wrapping sheet.

For a more complete understanding of this invention, reference will now be made to certain specific examples which indicate certain applications of this invention. However, it will be apparent that in its broader aspects this invention is not limited to the specific examples presented.

Example 1

Two fresh slices of Kraft Velveeta processed cheese measuring 2" by 2" by 3/8" were wrapped in absorbent tissue. On one flat surface of one of the pieces of covered cheese were placed 2 cc. of an aqueous phosphate buffer solution (pH 5.1) containing 35% cerelose (glucose). On one of the covered flat sides of the other piece of cheese were placed 2 cc. of an aqueous phosphate buffered (pH 5.1) enzyme solution of an enzyme containing about 35% cerelose. The glucose oxidase activity of the enzyme solution was about 175 glucose oxidase units per cc. while the catalase activity was about 60 catalase units per cc. These units were determined by that method essentially disclosed in Baker U. S. Patent No. 2,651,592 issued September 8, 1953. Both pieces of cheese were then given an outer wrapping of No. 54 DuPont moistureproof cellophane and both were refrigerated at about 5° C. for a period of six weeks. After this period both packages were opened and the surface of the cheese in the wrapper treated with the enzyme solution was light in color and apparently unchanged. The surface of the cheese without enzyme was definitely darker in color showing evidence of oxidation.

Example 2

An aqueous solution was prepared containing 10% carboxymethyl cellulose (CMC-70 Premium Low—water dispersible) and 5% glycerol as a plasticizer. To two parts of this solution was mixed one part of an enzyme solution comprising an aqueous phosphate buffer (pH 5.1) containing 35% cerelose and having a glucose oxidase activity of about 175 units per cc. and a catalase activity of about 60 units per cc. The resulting dispersion was then flowed over a sheet of moistureproof cellophane which was then held vertically and allowed to drain dry. This sheet product was suitable for use in wrapping cheese or other moist articles to prevent oxidative deterioration on account of exposure to atmospheric oxygen.

Example 3

A moistureproof cellophane sheet was coated on one surface with a carboxymethyl cellulose solution prepared in the same manner indicated in the previous example except that the initial solution of the binder prior to the addition of the enzyme solution contained 7.5% carboxymethyl cellulose and 7.5% of glycerol. After six months' storage at room temperature the dried paper still exhibited considerable catalase and glucose oxidase activity and was suitable as a wrapping paper to protect cheese from oxidative deterioration.

Example 4

A moistureproof cellophane sheet was treated on one surface with an aqueous solution of an enzyme having glucose oxidase and catalase activity and thereafter allowed to dry. As will be pointed out below, this product when compared against a control was effective for preventing the penetration of oxygen into a glucose-containing product covered with it.

Example 5

One pound of Kraft processed American cheese was melted in a double boiler. This cheese at a temperature of about 150° F. was poured into cardboard molds lined with enzyme-treated and control papers. These cheese packages were then sealed and refrigerated at about 5° C. The enzyme-treated paper was prepared by coating

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a moistureproof cellophane paper with an aqueous dispersion of polyvinyl alcohol and a plasticizer and a phosphate-buffered, glucose-containing enzyme solution having high glucose oxidase and catalase activities dispersed therein. The plasticizer in this instance was Santocizer B-16 (butyl phthalyl butyl glycolate). The control paper was prepared in the same manner except that the enzyme component was boiled in order to inactivate the enzyme. The treated surfaces of the papers were in direct contact with the cheese in each instance. After about six weeks' storage these packages were opened and examined. The sample treated with the enzyme-active coating was lighter and had a fresher appearance than the control which was somewhat yellowish.

In order to positively demonstrate in a quantitative manner the effectiveness of papers or other fabrics coated or impregnated in accordance with the process of this invention, the following experiment was devised. A glucose oxidase manometric assay substrate was prepared comprising an aqueous 0.1 molar solution of Na₂HPO₄ containing 3.3% cerelose (glucose) and 0.4% of the sodium salt of dehydroacetic acid (Dow's DHAS). This solution had a hydrogen ion concentration corresponding to pH 5.9. To this solution was added 0.2% agar and 0.5% of a 0.5% methylene blue solution. The resulting mixture was heated to dissolve the agar and 50 cc. portions were poured while warm into a series of 6" by 1" test tubes. The solution was covered with a layer of mineral oil and the tubes were placed in a boiling water bath to effect decolorization of the methylene blue. Thereafter the tubes were cooled to 50° C. and treated papers and control papers were fastened by an elastic band over the open ends of the tubes. The papers were positioned with the coated or treated side facing into the tube. Thereafter the tubes were inverted in order that the solution would come into direct contact with the paper. The tubes were then immersed in cold water to solidify the agar, whereafter the tubes were hung at room temperature to note any recoloration of the methylene blue due to the diffusion of oxygen through the paper and into the agar medium within the tube.

Utilizing this test procedure, papers prepared in accordance with Examples 3 and 4 above were tested, together with control papers. The control paper of Example 3 was the same as the test paper except that the coating contained no active enzyme. The control paper of Example 4 was uncoated. In the case of the control papers it was found that after 24 hours the methylene blue had recolorized in the tubes to a depth of 24 mm., after 48 hours to a depth of about 30 mm., and after 20 days the recolorization of the methylene blue due to oxidation was complete for the full depth of the agar layer. On the other hand, with the treated papers there was only very faint recoloration of the methylene blue even after 20 days and this occurred only immediately adjacent the interface between the coated paper and the agar substrate. This experiment conclusively demonstrates the ability of the catalase-glucose oxidase-coated paper in the presence of water and glucose to prevent the diffusion of oxygen into the article coated by the treated paper.

As indicated above, glucose should be incorporated with the enzyme employed for impregnating or coating the sheet in the event that glucose is not present in the moist solid material to be wrapped or covered with the paper. Likewise, under certain conditions, the catalase may be eliminated from the paper coating in the event that catalase is normally contained within the product wrapped. In order to obtain effective results under usual conditions, the amount of glucose oxidase present on the treated paper should be in excess of about 0.1 glucose oxidase units per square centimeter of the paper.

Also as previously indicated, this invention finds application in the packaging of frozen foods, particularly frozen fruits such as those which have a tendency to turn brown rapidly when thawing. Thus it is known that

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sliced frozen fresh peaches when thawed prior to use and while still wrapped in moistureproof but gas-permeable wrappings have a tendency to brown rapidly. This browning is due largely to the penetration of atmospheric oxygen into the package at a time when liquid water begins to form. This oxygen penetration is prevented by utilizing the treated sheet material of this invention since the glucose oxidase, catalase, glucose and water provide an effective oxygen barrier excluding the oxygen from the inner contents of the package.

In the foregoing it has been pointed out that glucose is necessary in the paper or in the substrate of the wrapped article in order to obtain the desired results. However, as pointed out in Reissue Patent No. 23,523, the glucose may initially occur as such or may be formed from polysaccharides, such as maltose, lactose, sucrose, dextrin or starch, by the activity of a specific enzyme which will convert these last mentioned materials to glucose. Thus such enzymes as maltase, lactase, invertase and diastase may be included in the enzyme system incorporated with the sheet material if desired.

It will be apparent from the foregoing considerations that many different kinds of papers or flexible sheet materials may be employed for applying the enzyme in accordance with this invention. Usually it is preferred to employ any type of moistureproof material, such as cellophane, wax paper, resin-treated papers, sheets of synthetics, such as Pliofilm, flexible styrene, polyethylene, cellulose resins, styrene resins, vinyl polymers, etc. Sheet materials of this character, while moistureproof, are somewhat permeable to oxygen and it is these gas-permeable and moistureproof fabric sheets which are of particular interest for the application of this invention.

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.

We claim:

1. A moist food product normally subject to oxidative deterioration upon contact with air having its exposed surface covered with a substantially moistureproof, gas-permeable sheet material, the interface between said material and said product containing glucose oxidase, catalase and glucose in sufficient quantities to convert any oxygen which may permeate said sheet to gluconic acid upon contact with said interface.

2. A moist food product normally subject to oxidative deterioration upon contact with air wrapped with a substantially moistureproof, gas-permeable fabric sheet, said sheet being coated on that surface in contact with

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said product with a water-dispersible binder and glucose oxidase and the interface between said sheet and said product containing glucose and catalase whereby oxygen diffusing from the air through said sheet reacts with said glucose to form a gluconic acid compound.

3. The invention recited in claim 2 wherein said product is cheese.

4. The invention recited in claim 2 wherein said product is a frozen food.

5. An article of manufacture comprising a packaged moist food normally subject to oxidative deterioration upon contact with gaseous oxygen having an exposed surface covered with a gas-permeable packaging material and having an interlayer between and in contact with said packaging material and said food, said interlayer providing an oxygen barrier which comprises water, glucose and glucose oxidase.

6. The article recited in claim 5 wherein said interlayer also includes catalase.

7. A gas-permeable sheet material having the enzyme glucose oxidase positioned on at least one exposed surface thereof in a concentration to provide an oxygen barrier when said material is contacted with a moisture-containing article in the presence of glucose.

8. The sheet material recited in claim 7 wherein the concentration of glucose oxidase is in excess of about one-tenth unit per square centimeter of said material.

9. A substantially moistureproof gas-permeable fabric sheet being coated on at least one surface with a water-dispersible binder and glucose oxidase in a concentration to provide an oxygen barrier when said surface is contacted with a moisture-containing article in the presence of glucose.

10. The sheet recited in claim 9 in which the coated surface also contains catalase.

11. The sheet recited in claim 10 in which the concentration of glucose oxidase is in excess of about one-tenth glucose oxidase unit per square centimeter of said coated surface.

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