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(54) PRESERVATION OF AGRICULTURAL PRODUCTS

(71) We, TSUKIHOSHI KASEI KABUSHIKI KAISHA (also known as MOON-STAR CHEMICAL CORPORATION), a corporation organised and existing under the laws of Japan, of 60, Shirayama-Machi, Kurume-Shi, Fukuoka-Ken, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates generally to the preservation of agricultural products. More particularly, the invention relates to compositions for surface coating for making possible the preservation of agricultural products over long periods, to a process for preserving agricultural products through the use of these compositions, and to agricultural products thus processed for preservation.

Among agricultural products, vegetables, fruits and cereals or grains, even during their storage after harvesting, carry on their living functions, absorb oxygen from the outside air to carry out a respiratory action, and continue vital functions and phenomena as they consume nutriment stored within their structures.

Vegetables, fruits, and cereals (hereinafter referred to as vegetables or the like) may be stored after harvesting in the fresh state for long periods preserving them in a state of low vital activity during which the consumption of stored nutriment in their structures is reduced to a minimum degree, and their structural compositions immediately after harvesting are maintained as much as possible.

In general, preservation for long periods can be accomplished by utilizing such principles as (1) the suppression of respiration; (2) the prevention of evaporation of water content, and (3) the prevention of a change of quality or deterioration due to microorganisms.

Examples in the prior art of the utilization of these principles in a specific form for prac-

tical preservation are (1) the suppression of respiration by low-temperature storage; (2) the suppression of respiration by lowering the partial pressure of oxygen in the preserving atmosphere; (3) the suppression of respiration and the prevention of evaporation of water content by packaging in film envelopes; and (4) the suppression of respiration and the prevention of evaporation of water content by coating the surfaces of the produce.

In the method (1) of suppressing respiration by low-temperature storage, the produce, or vegetable and the like, is preserved at as low a temperature as possible after harvesting without physiological damage due to low temperature with the aim of preserving the produce over a long period. In general, the respiratory activity of a plant becomes very low at temperatures close to 0°C, and the quantity of respiration increases 2 to 4 times with a temperature rise of 10°C; therefore, low temperature storage is a very effective measure for long term preservation. This method, however, requires great expense in installation of equipment, and, moreover, the maintenance of low-temperature conditions also adds to the operational costs. Furthermore, when, at the stage of transferring the commodity from cold storage to the consumer, the maintenance of cooling is interrupted and the temperature of the commodity is returned to the temperature of outside air, the surfaces of the vegetables and the like get wet due to dew collecting thereon, so that the product quality deteriorates rapidly.

In the method (2) of suppressing respiration by lowering the partial pressure of oxygen in the atmosphere surrounding the commodity, the property of plants such as vegetables is utilized whereby the amount of respiration varies with the partial pressure of oxygen in the surrounding atmosphere, becoming progressively smaller as the partial pressure of oxygen in the air becomes lower than 0.2 atmosphere, and decreasing rapidly when this

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partial pressure become less than 0.05 to 0.1 atmosphere. For example, the so-called CA (controlled atmosphere) storage method, wherein from a few percent to 20 percent of carbon dioxide gas is admixed into the air in the storage chamber of warehouse to lower the partial pressure of oxygen with the aim of long-period preservation, is regarded as a very good storage method. However, similarly to the above described low-temperature storage method, this CA storage method entails high costs for equipment and operation, and, furthermore, the beneficial effect of the preservation is lost by the return to the ordinary atmosphere in the distribution process subsequent to shipment from the storage warehouse.

In the method (3) of suppressing respiration and preventing moisture evaporation by packaging in a film envelope, vegetables and the like are stored in envelopes made of thin films of resins such as polyvinyl chloride, polyethylene and polypropylene. This method is initially effective in preservation in that, within the small, limited system in each envelope, the partial pressure of oxygen is lowered by the carbon dioxide gas exhaled by the contents of the envelope. However, the carbon dioxide gas thus discharged progressively accumulates in the envelope to cause so-called cumulative injury or damage, and, at a certain time, a sudden lowering of the product quality or decaying occurs. The thickness and material of the envelope film have been modified or the supplementary measure of aiding the flow of air by mechanically forming small holes therein has been adopted to overcome these disadvantages, but, as the degree of ripening of the vegetable or the like contained in the envelope progresses, fluctuations in the required oxygen quantity, the discharged carbon dioxide gas quantity, and, further, the quantity of moisture evaporated off occur, and it is extremely difficult to exercise fine control simultaneously over all of these conditions.

The method (4) of suppressing respiration and preventing moisture evaporation by surface coating has the following features. Ordinarily, a higher plant grown on land inhales oxygen necessary for cellular respiration from the outside and discharges carbon dioxide gas to the outside, the flowing in and discharging of gases necessary for respiration being accomplished through the epidermal cells having stigmas and lenticels. Therefore, by decreasing the cross-sectional areas of these stigmas and lenticels, the quantity of oxygen inhaled into the plant structure can be restricted without changing the partial pressure of the oxygen in the outside air, and, as a result, the quantity of respiration is reduced. Accordingly, as methods of utilizing this phenomenon for preservation, a large number of processes for coating films by some measure on the surfaces of vegetables and the like have been proposed. Examples of these proposals are contained in

Japanese Patent Publications Nos. 32344/1973, 946/1973, 18467/1973, 5030/1973, and 10683/1960 and United States Patents Nos. 2,700,025, 2,755,189, 2,872,325, 3,410,696, 2,961,322 and 2,346,755.

The processes proposed heretofore, generally comprise forming a film of hydrophobic wax or resin on the surface of the vegetables or the like in order to prevent a lowering of the degree of freshness thereof due to evaporation of the water content, or comprise forming a film of any of various synthetic resins on the surfaces of the vegetables or the like for the purpose of controllably suppressing the passage of gases, by utilizing the differences in gas permeability due to the molecular structures of the synthetic resins.

However, for accomplishing fine control of physiological functions in accordance with each and every kind of vegetable or the like by these proposed processes, an ample preservation effect would not be attained with films of uniformly standardized materials. For example, in the case where a film of very low gas permeability is formed to coat a vegetable or the like of relatively intense respirative action, and the minimum quantity of oxygen required for respiration cannot be inhaled in, the vegetable or the like undergoes anaerobic respiration, that is, respiration between molecules, and, as a metabolic product, alcohol is produced instead of carbon dioxide gas and water. As a result, an abnormal odour impairing the taste of the vegetable or the like as food is generated, and the object of preservation cannot be achieved. On the other hand, in the opposite case wherein a film of relatively high gas permeability is formed to coat a vegetable or the like with a small respiration capacity, the gas necessary for respiration freely flows in, and the effect of preservation due to the film is not exhibited.

Thus, for example an egg, which is regarded herein as one agricultural product, comprises a blastodisc or embryo, egg white or albumen, egg yolk and an eggshell. The eggshell has numerous micropores, through which moisture and carbon dioxide gas are discharged to the outside during storage, and, at the same time, microorganisms are able to infect the egg from the outside through these micropores. The evaporation of moisture from an egg is principally the evaporation of the water in the albumen to the outside, and this gives rise to a decrease in the weight of the egg, an expansion of the air shell, and a lowering of the product quality. Furthermore, when the carbon dioxide gas dissolved in the albumen penetrates to the outside, the pH rises, and it becomes impossible to prevent the propagation in the egg of the microorganisms which have infected the egg from the outside. Consequently, the preservability of the egg decreases remarkably.

The principles of the long-term preservation of the eggs of fowl such as chickens and

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quails, which eggs after being laid are used especially for food, are substantially the same as those in the case of vegetables and the like, the important measures based on these principles being: (1) the suppression of the exhalation of carbon dioxide gas to the outside; (2) the prevention of the evaporation of moisture; and (3) the prevention of infection and the propagation of microorganisms.

Examples of preservation methods based on these principles and heretofore proposed are: (1) the prevention of infection and the propagation of microorganisms by low-temperature storage; and (2) the suppression of the exhalation of carbon dioxide gas to the outside, the prevention of the evaporation of moisture, and the prevention of infection by microorganisms through surface coating.

Method (1) comprises conveying laid eggs to an egg storage chamber at a low temperature, carrying out processes such as inspection, washing and classification of the eggs, packaging the eggs in boxes, transporting the eggs thus packaged to consumption areas by refrigerated trucks, vans or lorries, and carrying the eggs to refrigerated show-cases of retail stores. In an imperfect distribution system, such as those existing at present, however, water vapour in the atmosphere condenses on the egg shells when the eggs contact the outside air during distribution, and, as a consequent, the eggs assume a state resembling perspiration or sweating. The net result, contrary to expectation, is that the preservability is lowered. Furthermore, this method tends to be excessively expensive and is difficult to implement under the present circumstances.

Method (2) comprises coating the surfaces of eggs with a film to preserve the eggs by using the properties of the film. For this purpose, a number of processes have been proposed, examples of which are disclosed in Japanese Patent Publications Nos. 5027/1957, 6226/1969 and 20150/1968. These known processes are characterized by the forming on the egg surface of a film of a hydrophobic material such as wax or paraffin for the purpose of preventing the lowering of the freshness of the egg due to evaporation of water or by the formation on the egg surface of a film of any of various synthetic resins for the purpose of controllably suppressing the passage of gases, the differences in gas permeabilities due to the molecular structures of these synthetic resins being utilised. By these processes, however, control of the discharge of the carbon dioxide gas of the egg to the outside, the evaporation of water, and the prevention of infection and propagation of microorganisms would not be accomplished simultaneously and efficiently. This problem is substantially the same as that described with respect to vegetables and the like.

It is an object of this invention to provide a process for coating the surfaces of agricul-

tural products for the purpose of controlling simultaneously and comprehensively the quantity of oxygen required for respiration, the quantity of discharged carbon dioxide gas, and the quantity of water evaporation at the time of storage of the agricultural products, in accordance with the respective characters thereof to maintain the agricultural products in a high degree of preservation over a long period of time; a coating composition suitable for use in this process; and agricultural products thus coated.

Another object of the invention is to provide agricultural products which are not subject to any lowering of their degree of freshness in their distribution route from their preservation processing, through their reception by the consumers, to their use in cooking; a process for processing these agricultural products, and a coating composition suitable for use in this process.

Still another object of the invention is to provide an economical process for preserving agricultural products which does not require any preserving equipment, management cost, maintenance cost, and other expense; a coating composition suitable for use in this process; and preservation processed agricultural products thus obtained.

According to one aspect of this invention there is provided a composition for the preservation processing of agricultural products which carry on living functions after harvesting selected from the group consisting of fruits, vegetables, eggs and grains, comprising a dispersion of microparticles as a dispersoid of a hydrophobic substance selected from the group consisting of natural waxes, vegetable fatty oils, hydrogenated fatty oils and mineral oils in an aqueous solution as a dispersion medium of a water-soluble high polymer and a dispersing agent, said water-soluble high polymer being selected from the group consisting of polysaccharides, polysaccharide derivatives, proteins, alginates, and polyvinyl alcohols, in said composition the weight ratio of said hydrophobic substance and said water-soluble high polymer being from 10:0.2 to 10:3, the composition being capable of application as a coating layer to cover the outer surface of an agricultural product and of being dried to form a coating membrane comprising the microparticles dispersed in a matrix of the membrane of the water-soluble high polymer which has been in aqueous solution and having fine continuous microvoids formed between the microparticles and the matrix, the membrane controllably suppressing the respiration of the agricultural product.

According to another aspect of this invention there is provided a process for preservation of agricultural products which carry on living functions after harvesting selected from the group consisting of fruits, vegetables, eggs and grains, which comprises applying a dis-

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(3)

persion as a coating layer to cover the outer surface of an agricultural product, the dispersion being prepared by dispersing a hydrophobic substance selected from the group consisting of natural waxes, vegetable fatty oils, hydrogenated fatty oils and mineral oils in the form of microparticles in an aqueous solution of a water-soluble high polymer and a dispersing agent constituting a dispersion medium; said water-soluble high polymer being selected from the group consisting of polysaccharides, polysaccharide derivatives, proteins, alginates, and polyvinyl alcohols, in said composition the weight ratio of said hydrophobic substance and said water-soluble high polymer being from 10:0.2 to 10:3; and drying the dispersion thus applied to form a coating membrane comprising the microparticles dispersed in a matrix of the membrane of the water-soluble high polymer which has been in the aqueous solution and having fine continuous microvoids formed between the microparticles and the matrix, thereby controllably to suppress the respiration of the agricultural product.

According to a further aspect of this invention there is provided a preservation-processed agricultural product which comprises: (a) an agricultural product which carries on living functions after harvesting selected from the group consisting of fruits, vegetables, eggs and grains, and (b) a membrane covering the outer surface of the agricultural product, and comprising a water-soluble high polymer substance constituting a matrix and microparticles of a hydrophobic substance dispersed in the matrix; the hydrophobic substance being selected from the group consisting of natural waxes, vegetable fatty oils, hydrogenated fatty oils and mineral oils, and the water-soluble high polymer being selected from the group consisting of polysaccharides, polysaccharide derivatives, proteins, alginates and polyvinyl alcohols; in said membrane the weight ratio of said hydrophobic substance and said water-soluble high polymer being from 10:0.2 to 10:3; the membrane having fine continuous microvoids between the matrix and the microparticles and thereby controllably suppressing the respiration of the agricultural product itself.

The coating composition of the invention when applied to the surface of an agricultural product dries to form a coating membrane which comprises fine particles of the hydrophobic substance (referred to herein as "microparticles") dispersed in a matrix of the membrane of the water-soluble high polymer which has been in the aqueous solution, continuous microvoids being formed between the fine particles of the dispersoid (or "microparticles") and the matrix. The agricultural product which has been coated in this way can be preserved in a fresh state over a long period because its respiration is controllably suppressed by the membrane, and can only take place through

the continuous microvoids just referred to.

The term "water-soluble high polymer" is used herein to designate a natural or synthetic high polymer having a hydrophilic group such as a hydroxyl group, a carboxyl group, or an amino group and which, upon being dissolved in water, undergoes hydration through the abovementioned hydrophilic group to become a colloidal aqueous solution or to assume a gel state.

The term "hydrophobic substance" is used herein to designate a material which is substantially insoluble in water and in which water is substantially insoluble. The material can be a solid or a substantially non-volatile liquid.

Various features and advantages of this invention will be more clearly apparent from the following detailed description and accompanying drawing, beginning with a consideration of general features of the invention and concluding with specific examples of practice illustrating preferred embodiments of the invention.

In the drawing:

FIG. 1 is a perspective view of an apple which has been preservation processed in accordance with the invention, the left-hand half of the drawing showing the outside of the apple and the right-hand half showing the state in which the coating membrane has been peeled off and, moreover, showing the membrane in axial section; and

FIG. 2 is a fragmentary, enlarged, diagrammatic view in section taken along a plane perpendicular to the membrane shown in FIG. 1, and showing a region in the vicinity of the apple epidermis.

The coating composition of this invention and the membrane formed thereby on the surface of an agricultural product will first be described with reference to the drawing.

Referring to FIG. 1, the agricultural product 1, which is an apple in this example, and which has been processed in accordance with this invention, has thereon a coating membrane 2 formed by applying the dispersion of this invention as a coating thereon and drying the coating.

A coating composition comprising an aqueous solution of a water-soluble high polymer and fine particles of a hydrophobic solid or a hydrophobic and non-volatile liquid of low affinity for the water-soluble high polymer uniformly mixed and dispersed in the aqueous solution is applied as a coating layer and dried on the outer surface of the agricultural product 1. The water which is the solvent of the solution of the water-soluble high polymer and, at the same time, is the dispersion medium for the hydrophobic substance progressively evaporates, and the fine particles of the dispersoid gradually approach one another and begin to form a membrane.

In this case, since the outer surfaces of these

5 fine particles (or microparticles) are sur-
rounded by the solution of the water-soluble
high polymer of low affinity for these particles,
the microparticles themselves do not "sinter"
or cohere into a continuous film as in the case,
for example, of the rubber particles of a rub-
ber latex, but are in a discrete state in which
the solution of water-soluble high polymer in
the concentrated state is interposed between
the microparticles.

10 Reference is now made to FIG. 2. The
microstructure of the coating membrane for
preservation which has been formed in this
manner is shown together with the microstruc-
ture of the epidermis of an apple in FIG. 2,
in which the coating membrane formed after
drying is designated by reference numeral 2,
and reference numeral 3 designates one portion
of the epidermis cell layer of the apple 1
(FIG. 1).

20 About the time when most of the water
content has evaporated off, the microparticles
lose their fluidity. This structural state is
analogous to that of a wall formed by stacked
stones and having voids filled with water. With
the lapse of time, as the coating layer exists
in this state, the solution of the water-soluble
high polymer finally becomes fully dry to form
a continuous membrane 2. However, since the
dispersoid particles or microparticles 4 are sur-
rounded by a matrix of the water-soluble high
polymer 6, the evaporation of the water and
the drying give rise to a "shrinkage" of the
solution of water-soluble high polymer due to
a reduction in the volume of the solution of
the water-soluble high polymer, whereby ex-
tremely minute and, moreover, continuous or
intercommunicative microvoids 5 are produced
between the matrix of the water-soluble high
polymer 6 and the microparticles 4.

35 These microvoids 5 are mutually intercom-
municative or continuous and form tortuous
passageways 7 for the passage of gases between
the side of the membrane contacting the apple
epidermis 3 and the side contacting the outer
atmospheric air. Since the microvoids 5 are
dispersed three-dimensionally and are mutually
intercommunicative throughout the coating
membrane 2, the passageways for the passage
of gases formed by the intercommunication of
the microvoids also exist three-dimensionally
in the coating membrane, and, moreover,
there is a high possibility of mutual intercom-
munication between these passageways. There-
fore, it may be said that this group of passage-
ways forms a three-dimensional labyrinth (i.e.,
the passageways are curved also in directions
perpendicular to the plane of the drawing).

60 The epidermis 3 of the apple in contact with
this coating membrane comprises a large num-
ber of cells 8 and stigmas 9 between the cells.
The effective diameters and the distribution
density of the passageways 7 for the passage
of gases existing in the coating membrane 2
are respectively very much smaller than, and

larger than, the diameters and distribution
density of the stigmas in the apple epidermis
3. Therefore, the desired degree of gas per-
meability can be positively maintained even
when the passageways 7 for gas passage and
the stigmas 9, respectively, have random dis-
tributions.

Even if the dispersoid is in the form of
minute liquid oil droplets at room temperature
at this time, since this dispersoid is enveloped
in a thin wall of the water-soluble high poly-
mer, the oil droplets will not cohere into a
continuous oil film even after the water con-
tent has completely evaporated off, but in-
dividual oil particles will retain their particu-
late shape.

75 We have found that, if, in the practice of
this invention, the quantity of the water-soluble
high polymer is excessive relative to the quan-
tity of microparticles of dispersoid, these par-
ticles will be fully surrounded by the matrix
of the water-soluble high polymer and will be
in an excessively discrete state, whereby con-
tinuous microvoids cannot be formed between
the particles and the matrix of water-soluble
high polymer. On the other hand, if the quan-
tity of the water-soluble high polymer is too
small, the ability to form the continuous mem-
brane becomes poor. In order to produce con-
tinuous microvoids in this case, the ratio of
the weight of the dispersoid to the weight of
the high polymer substance should be in the
range of from 10:0.2 to 10:3, as can be seen
from specific examples 1 to 11 below. The
size of the continuous microvoids decreases
with a decrease in the grain size of the dis-
persoid particles and, furthermore, as the ratio
of the volume of the dispersoid to that of the
water-soluble high polymer approaches the
minimum limit for the formation of micro-
voids.

Through these microvoids, oxygen required
for the minimum respirative action so that the
agricultural product will not be subject to
physiological damage is supplied, and, at the
same time, waste gases and moisture are dis-
charged to the outside, whereby a maximum
preservation effect is exhibited. For this pur-
pose, the particle size of the dispersoid or, in
other words, the particle size of the hydro-
phobic substance should be in the range of
from 0.1 to 10 microns, preferably from 1 to
8 microns. For causing the particle size of the
dispersoid to fall in a desired range, various
measures which may be adopted for the control
of the particle size of the dispersoid in aqueous
emulsions or aqueous suspensions can be used.

More specifically, examples of such measures
are: the use of an emulsifier or a suspension
stabilizer; the choice of an appropriate concen-
tration or viscosity of the dispersion medium,
i.e., the aqueous solution of the water-soluble
high polymer; the choice of an appropriate
weight ratio of (water-soluble high polymer
to be used)/(hydrophobic substance to be

used); the adjustment of the rotational speed and time period of agitation during the preparation of the dispersion; the choice of an appropriate difference between the solubility parameters of the water-soluble high polymer and the hydrophobic substance; and the use of a hydrophobic substance of desired particle size in the case where the substance is a solid.

As an emulsifier, a (C_{16-18}) fatty acid mono-, di- or triester of a sucrose, preferably a C_{16-18} fatty acid ester, lecithin or an alkali metal salt (Na or K salt) of oleic acid may be used in a proportion of from 0.2 to 10 percent by weight relative to the hydrophobic substance to be dispersed. In connection with sucrose fatty acid esters, reference may be made to Ind. Eng. Chem. 48, 1459-14621 (1956).

In order to obtain the dispersion, the emulsifier is first dissolved in the required quantity of warm water, and the hydrophobic substance to be dispersed is heated in the case where it is a solid at room temperature to a temperature above its melting point to form a liquid, and is poured into the warm water, as it is agitated at a rotational speed of from 1,000 to 6,000 rpm., the agitation being continued until a desired particle size is obtained.

In this process, the water-soluble high polymer may be dissolved beforehand in the warm water, and the hydrophobic substance dispersed therein. Alternatively, the water-soluble high polymer may be added to and dissolved in the previously prepared aqueous emulsion or suspension of the hydrophobic substance. When used for a coating process, the coating composition or the dispersion is from 3 to 50 cps in terms of viscosity, and the content of the hydrophobic substance is from 3 to 20 percent by weight, preferably from 5 to 15 percent by weight. A higher viscosity or concentration is of course feasible and is preferable to reduce the volume of the coating composition or the dispersion.

The coating composition or the dispersion can be applied to an agricultural product by any method which is commonly used or is usable for applying liquid coating material. Examples of specific methods are spray coating, flow coating and brush coating of the dispersion onto the agricultural product; and immersing the agricultural product in a bath of the dispersion. The drying after coating can be carried out by any suitable drying method at room temperature and atmospheric pressure or with slight heating and/or under reduced pressure.

After drying, the thickness of the resulting membrane is from 3 to 100 microns, particularly from 3 to 20 microns. The water vapour permeability and the oxygen permeability of this membrane are respectively from 20 to 600 grams/square meter/24 hours ($g./m^2./24hr.$)/atm. ($20^\circ C$ dry) and from 35 to 1,200 $g./m^2./24hr./atm$ ($20^\circ C$ dry).

Materials suitable for use in the practice of this invention are as follows. Examples of suitable materials for the water-soluble high polymer are: pentosans (e.g., acacia or gum arabic); hexosans (e.g., starches, fructosans and mannosans) polysaccharides such as conjugated polysaccharides (e.g., gums); proteins such as casein, gelatin, and soybean protein, cellulose derivatives such as methylcellulose and carboxymethylcellulose, preferably the sodium salt; sea-weed mucilages such as alginates, preferably the sodium salt (e.g., agar-agar), and polyvinyl alcohols. The solubility parameters of these materials are from 13 to 21. For example, the solubility parameters of acacia and casein, which are used most often in the Examples of this invention, are 17.2 and 15.4, respectively. Since the solubility parameters of these high polymers are close to that of water, i.e. 21, they are water-soluble in all cases. In connection with "solubility parameters" reference may be made to Joel H. Hildebrand and Robert L. Scott, "The Solubility of Nonelectrolytes", Third Edition, Dover Publications, Inc., New York, 1964, pp. 119-129 and pp. 435-439.

Examples of the hydrophobic substance include natural waxes such as beeswax and carnauba wax, vegetable oils such as soybean oil and coconut oil, and hardened oil resulting from the hydrogenation of such vegetable oils and mineral oils as paraffin and microcrystalline paraffin. The solubility parameters of these materials are from 5 to 10, which are far from that of water. Therefore, each of these materials is not water-soluble and is thus hydrophobic. The difference between the solubility parameters of the water-soluble high polymer and hydrophobic substance used is ordinarily from 3 to 15, particularly from 5 to 13.

The above listed water-soluble high polymers and hydrophobic substances, exclusive of mineral oils, do not have any deleterious effect on the human body and are authorised by the Ministry of Health and Welfare of the Japanese Government as being edible or usable in or as food additives. Accordingly, these substances do not create any problems of hygiene or sanitation when they are brought into contact with the outer surfaces of vegetables and the like.

It is possible that, among the mineral oils, there are some which can impart harmful effects to the human body if absorbed therein in large quantity. However, as described hereinbefore, the microparticles of the hydrophobic substances are completely surrounded by the dispersion medium in the formation of the membrane, so that there is no possibility of a mineral oil of the dispersoid penetrating through the epidermis of the vegetable or the like into the interior thereof, and, in the case where the product is to be used after peeling, for example, in the case of fruits for canning,

these mineral oils can be used with an ample margin of safety.

In addition to the choice of the mixing ratio of the water-soluble high polymer and the hydrophobic substance in the control of the quantity of respiration, i.e., the quantity of permeation of oxygen, measures such as adjusting the membrane thickness by appropriate choice of the content of the hydrophobic substance and control of the adhering quantity by regulating the viscosity of the dispersion can be carried out, but it is advantageous in actual practice to verify beforehand the blending ratios which will permit the formation of a membrane of the desired porosity and, moreover, will result in a maximum rate of drying.

In comparison with the prior techniques of preservation of agricultural products, the present invention has numerous advantageous features, the most important of which are set forth below:

1. A first advantage will be described through a comparison with the "pretreatment" generally practised for fruits and vegetables. This "pretreatment" is a method of suppressing respiration and of suppressing water evaporation by utilising the physiological characteristics of the products. Immediately after harvesting, the fruits and vegetables are exposed in a cool place with good ventilation for a period of several hours to several days so as to promote the drying of the epidermis, for the stigmas and lenticels to contract, and thereby to suppress respiration and water evaporation. However, a problem accompanying this "pretreatment" is that, as the humidity of the surrounding air rises, the stigmas and lenticels again expand or give rise to the so-called "reswelling of peel" phenomenon, whereby the effect of preservation is lost.

In contrast, the process for the preservation of an agricultural product according to this invention comprises physically forming a membrane having fine continuous microvoids on the epidermis of the fruits and vegetables. These microvoids of the membrane formed on the agricultural product which have been preservation processed in this way undergo no deformation even when the humidity of the surrounding air varies, and the preservation effect can be continued constantly.

2. The second advantageous feature is that, since the quantity of oxygen required for respiration, the quantity of discharged carbon dioxide gas, and the quantity of evaporated water at the time of storage of an agricultural product can be controllably suppressed precisely, simultaneously, and, moreover, in a comprehensive manner in accordance with the physiological functions of the agricultural product through the action of the fine continuous microvoids, a very high degree of product preservation in comparison with that resulting from conventional methods, in which these quantities are suppressed separately, can be

continuously maintained over a long period.

3. A third advantageous feature is that, since the membrane of this invention having fine continuous microvoids is formed as a coating directly on the outer surface of an agricultural product, the agricultural product thus processed according to this invention is not subjected to an interruption of its state of preservation during its distribution operation as in the known low-temperature storage method, (or the CA storage method), and there is no loss whatsoever of the preservation effect until the consumer begins to prepare the product for use.

4. A fourth advantageous feature is that, since preservation is fully effected merely by forming a membrane having fine continuous microvoids as a coating on the outer surface of an agricultural product, there is no need whatsoever for facilities such as storage warehouses or chambers for preservation, so that the management and maintenance costs thereof are eliminated, and, furthermore, the coating process can be carried out by a very simple procedure such as spraying and immersion, whereby the process does not require much labour and is economical.

While the composition for the preservation processing of agricultural products according to this invention is ordinarily placed on the market in a state wherein it can be used immediately, it can be placed on the market in a concentrated form to be subsequently diluted for use by the user or in the form of a kit comprising in combination an aqueous solution of the water soluble high polymer material and an aqueous dispersion (particularly an emulsion) of the hydrophobic substance to be subsequently mixed for use by the user. Such methods of marketing are particularly advantageous and effective for long-term preservation of the composition.

In order to indicate more fully the nature and advantages of this invention, the following specific examples of practice constituting preferred embodiments of the invention are set forth, it being understood that these examples are presented as illustrative only and that they are not intended to limit the scope of the invention:

Example 1.

The following materials were used in the quantities specified and in the manner described below.

	Parts by weight	
hydrogenated coconut oil	15	
casein	2	
sodium oleate	0.75	
(or sucrose fatty acid (C ₁₆ —C ₁₈) ester	1.5)	125
water	100	

The sodium oleate or sucrose fatty acid

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ester, which may optionally be a mono-, di- or triester was dissolved as an emulsifier in the water, and, as the resulting solution was heated at 60°C, the casein was dissolved therein. Then, as the resulting solution was stirred by an agitator operated at 6,000 rpm., hydrogenated coconut oil heated and melted at 60°C was poured in to prepare a uniform suspension. The particle size of the particles in the suspension thus prepared was substantially 1 micron with both emulsifiers.

In this suspension, "Unshū" mandarin oranges or tangerines (*Citrus unshū*) were immersed for 1 or 2 seconds and dried in an air stream to form a membrane on the outer surface thereof. These "Unshū" oranges were stored at room temperature for 60 days and compared with similar "Unshū" oranges without surface treatment stored under the same conditions as a reference or control. The results were as follows:

	Citric acid (%)	Brix (°)	Weight loss (%)
Oranges according to this invention	1.02 (1.23)	11.2 (9.6)	10.9
Control oranges	0.80 (1.23)	8.8 (9.6)	20.3

Note: the values in parentheses are those at the start of the test.

As is apparent from the above results, the oranges processed in accordance with this invention underwent less variation in citric acid content, degrees brix and weight than the control oranges and, therefore, exhibited better results.

The instant test was started with oranges of a uniform degree of ripeness of 50 percent. The oranges processed according to this invention exhibited a residual green colour of the order of 20 percent, no wilting, and a good exterior appearance, while all of the control oranges exhibited an over-ripe state with extreme wilting and had no value as a marketable commodity.

Sucrose (C₁₆₋₁₈) fatty acid (mono-, di- and tri-) esters are prescribed as edible emulsifiers by the law on food and drugs in Japan. The structure depends on the degree of esterification found to be desirable in use. However, since even purified emulsifiers can be contaminated with some residues of materials used in their manufacture such as catalysts and solvents, any effects of such residues on the human body when absorbed therein should be fully considered when a particular emulsifier is to be chosen. In Japan, sucrose fatty acid esters are permitted in the food industry when no dimethylformamide used as a solvent in the manufacture thereof can be detected; however, in the United States of America and amongst countries of the European Economic Community (EEC), sucrose fatty acid esters have not been prescribed as additives for foods and cannot be used as emulsifiers in the practice of the present invention in those countries.

Sodium oleate has a permitted use in Japan as a coating agent only for fruits and fruit-like vegetables having an epidermis such as tomatoes.

Accordingly, the emulsifier of the present invention should be so chosen and used as to be subject to the laws and ordinances on foods and drugs in the particular country in which the present invention is to be practised.

Sucrose fatty acid esters are less effective as an emulsifier than sodium oleate, and should thus be used in a larger quantity as compared with the case of sodium oleate. For some kinds of mandarin oranges or apples, the oils or fats contained therein can bleed on to their epidermis, and the membrane produced in accordance with the present invention from a coating dispersion in which a sucrose fatty acid is used cannot be satisfactorily formed in some cases.

The above description of the choice of emulsifier is also relevant to Examples 2 to 11.

Example 2.

The following materials were used in the quantities specified and in the manner described below:

	Parts by weight	
coconut oil (SP*: 9.8)	15	
starch (SP: 19.70)	1.5	
sodium oleate	1.2	
(or sucrose fatty acid ester	1.5)	
water	100	90

*Solubility Parameter

An emulsion of the coconut oil was prepared by the procedure specified in Example 1. The grain size of the particles in the finished emulsion was 0.7 micron with both emulsifiers.

"Saya-endo" pod legumes similar to field peas (*Pisum arvense*), were immersed for 1

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5 to 2 seconds in this emulsion, and the emulsion coating was dried in a stream of air to form a coating membrane on the outer surfaces of the peas. The coated peas were stored at room temperature and their weight loss (%)

and external appearance were compared with those of peas without surface treatment stored under the same conditions as a reference or control, whereupon the following results were obtained.

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After -----	Weight loss (%)	
	"Saya-endo" of invention	Control "saya-endo"
1st. day	9.1	16.0
2nd. day	12.6	32.6
3rd. day	18.6	49.6
4th. day	24.8	62.0
6th. day	36.0	75.0
8th. day	47.3	81.5

15 As is apparent from the above results, the loss in weight of the "saya-endo" peas processed according to this invention was less than that of the control peas. Furthermore, the peas processed according to the invention exhibited only some wilting after 8 days, but consider-

able wilting was observed in the control peas after 3 days.

Example 3.

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The following recipe was used to prepare a suspension of beeswax by the procedure set forth in Example 1.

Parts by weight

25	beeswax (SP: 8.0)	10
	casein (SP: 15.4)	2
	sodium oleate	0.5
	(or sucrose fatty acid ester	1)
	water	100

30 The grain size of the particles in the suspension thus prepared was 3 microns with both emulsifiers.

35 Apples were immersed in this suspension for 1 to 2 seconds and were then dried in a stream of air to form a membrane covering the outer surfaces of the apples. The apples were then

stored at room temperature for 142 days and compared with control apples without surface processing but stored under the same conditions with respect to malic acid content, degrees brix and loss in weight. The results were as follows:

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	Malic acid (%)	Brix (°)	Weight loss (%)
Apples according to the invention	0.34 (0.36)	11.7 (11.9)	8.0
Control apples	0.28 (0.36)	10.1 (11.9)	19.2

Note: Values within parentheses are those at the start of the test.

45 As is indicated by the above results, the apples processed in accordance with this invention exhibited better results than the control apples with respect to malic acid content, degrees brix and weight loss. Furthermore, the

apples processed according to the invention did not show any change in both sarcocarp hardness and lustre during storage, but, in contrast, the control apples exhibited severe wilting and a great change in lustre.

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Example 4.

A soybean oil emulsion was prepared by the procedure specified in Example 1 with the following recipe:

5		Parts by weight
	soybean oil (SP: 9.8)	10
	carboxymethylcellulose, Na (SP: 21.05)	0.5
	sodium oleate	0.8
10	(or sucrose fatty acid ester	1)
	water	100

The grain size of the particles in the emulsion thus prepared was 5 microns with both emulsifiers.

In this emulsion, "sora-mame" flat broad beans similar to lima beans, were immersed for 1 to 2 seconds and were then dried in a stream of air to form a membrane covering the outer surface of each bean. The beans thus processed were then stored at room temperature, and their weight loss (%) and external appearance were compared with those of control beans without surface processing but stored under the same conditions. The results were as follows.

After -----	Weight loss (%)	
	Beans of the invention	Control beans
1st. day	2.9	6.3
2nd. day	6.1	13.0
3rd. day	10.1	20.1
4th. day	15.7	28.1
6th. day	24.8	45.5
8th. day	28.0	57.2

As indicated by the above results, the beans processed according to the invention exhibited better results in weight loss than the control beans. Furthermore, while the beans processed according to the invention wilted after 6 days and were observed to have blackened somewhat after 8 days, the control beans had

already wilted after 3 days and blackened after 4 days.

Example 5.

A suspension of beeswax was prepared by the procedure set forth in Example 1 with the following recipe.

40		Parts by weight
	beeswax	10
	acacia (gum arabic) (SP: 17.2)	2
	sodium oleate	0.8
	(or sucrose fatty acid ester	1)
45	water	100

The grain size of the particles in the suspension thus prepared was 8 microns with both emulsifiers.

In this suspension, tomatoes with a degree of ripeness (see Journal of Food Science, 39, pp. 701—703 (1974) of substantially 20 percent were immersed for 1 to 2 seconds and were then dried in a stream of air to form a

membrane covering the outer surface of each tomato. The tomatoes thus processed were then stored at room temperature, and their weight loss (%) and external appearance were compared with those of control tomatoes without surface processing but stored under the same conditions. The results were as follows:

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After-----	Weight loss (%)	
	Tomatoes of the invention	Control tomatoes
1st. day	0.89	0.91
2nd. day	1.28	1.69
3rd. day	1.87	2.57
4th. day	2.56	3.22
5th. day	3.58	4.44

As indicated by the above results, the tomatoes processed according to the invention exhibited better results in weight loss than the control tomatoes. Furthermore, the degree of after-ripening, that is, acquiring of colour, during storage of the tomatoes processed according to the invention was from 3 to 5 days slower than that of the control tomatoes, and the distribution time, i.e. the marketing or

saleable time, could be prolonged by the number of days thus extended.

Example 6.

An emulsion was prepared by the procedure specified in Example 1 with the coconut oil and aqueous solution of sodium alginate of the following recipe used as the dispersoid and the dispersion medium, respectively.

Parts by weight

coconut oil	10
sodium alginate (SP: 21.84)	0.2
sodium oleate	0.8
(or sucrose fatty acid ester	1)
water	100

The grain size of the particles in the emulsion thus prepared was 0.3 micron with both emulsifiers.

In this emulsion, "nashi" or Japanese pears (*P. serotina* var. *culta*) were immersed for 1 to 2 seconds and were then dried in a stream of air to form a membrane covering the outer

surface of each pear. The pears thus processed were then stored at room temperature, and their weight loss (%) and external appearance were compared with those of control pears without surface processing but stored under the same conditions, whereupon the following results were obtained.

After ---	Weight loss (%)	
	Pears of the invention	Control pears
10 days	6.27	9.73
21 days	11.27	17.21

As indicated by these results, the pears processed according to the invention exhibited better results in weight loss than the control pears. Furthermore, after 21 days of storage, the pears processed according to the invention exhibited no decrease in lustre and showed no wilting or shrivelling, whereas the control pears exhibited a loss of lustre and wilting or shrivelling.

Example 7.

An emulsion was prepared by the procedure specified in Example 1 with a mixture of the

coconut oil and beeswax of the following recipe.

Parts by weight

coconut oil	5	55
beeswax	5	
sodium oleate	0.8	60
(or sucrose fatty acid ester	1)	
("konnyaku"*) mannan	2	
water	100	

*) devil's tongue jelly

The grain size of the particles in the emulsion thus prepared was 4 microns with both emulsifiers.

- 5 In this emulsion, "hakuto" or peaches were immersed for 1 to 2 seconds and then dried in a stream of air to form a membrane covering the outer surface of each peach. The peaches

thus processed were stored at room temperature, and their weight loss (%) and external appearance were compared with those of control peaches without surface processing but stored under the same conditions, whereup the following results were obtained.

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After ---	Weight loss (%)	
	Peaches of the invention	Control peaches
2 days	2.85	4.21
5 days	5.00	6.55
10 days	6.99	11.32

- 15 As indicated by these results, the peaches processed according to the invention exhibited better results in weight loss than the control peaches. Furthermore, no variation in the sarcocarp and no loss of lustre whatsoever were observable in the peaches processed according to the invention, whereas the control peaches

showed a beginning of browning, coarsening of the sarcocarp and some loss of lustre.

Example 8.

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An emulsion of coconut oil was prepared by the procedure specified in Example 1 with the following recipe.

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Parts by weight

30	coconut oil	10
	casein	2
	sodium oleate	0.5
	(or sucrose fatty acid ester	1.5)
	water	100

- 35 The grain size of the particles in the emulsion thus prepared was 2 microns with both emulsifiers.

- 40 In this emulsion, chicken eggs were immersed for 1 to 2 seconds and were then dried in a stream of air to form a membrane covering the outer surface of each egg. The eggs

thus processed were stored at room temperature for 35 days, during which their specific gravity, pH value, yolk index, and albumen index and weight loss % at different times were compared with those of unprocessed control chicken eggs. The results obtained were as follows:

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	Eggs of the invention	Control eggs
Specific gravity---		
Start of test	1.083	1.083
After 20 days	1.077	1.055
After 35 days	1.073	1.032
pH value---		
Start of test	9.0	9.0
After 20 days	8.6	9.0
After 35 days	8.3	8.9
Yolk index---		
Start of test	0.39	0.39
After 20 days	0.29	0.14
After 35 days	0.26	0.10
Albumen index---		
Start of test	0.04	0.04
After 20 days	0.04	$\frac{2}{3}$ 0
After 30 days	0.03	$\frac{2}{3}$ 0
Weight loss (%) ---		
After 20 days	1.6	2.6
After 30 days	2.0	3.5
After 40 days	2.5	4.7
After 50 days	3.6	5.7
After 60 days	3.7	6.7

The yolk index of each egg was determined by pouring the contents of the egg onto a flat plate, measuring the height and diameter of the yolk without separation of the albumen and yolk, and dividing the yolk height by its diameter. The albumen index is similarly determined by pouring the contents of the egg onto a flat plate and dividing the measured albumen height by its diameter.

From the above results, it is apparent that the process of the invention is highly effective in preserving eggs in a better state in all respects than unprocessed eggs.

Example 9.

A suspension of beeswax was prepared by the procedure specified in Example 1 with the following recipe.

Parts by weight

beeswax	10	20
gelatine	3	
sodium oleate	0.5	
(or sucrose fatty acid ester	1)	
water	100	

The grain size of the particles in the suspension thus prepared was 1 micron with both emulsifiers.

In this suspension, ears of Indian corn (maize) immediately after harvesting, and in their harvested state without husking, were immersed over 2/3rds of their overall lengths from their stem ends for 1 to 2 seconds, and were then dried in a stream of air to form a membrane covering the surfaces thus immersed.

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The ears of corn were stored at room temperature, and their degree brix and weight loss at different times were compared with those of

unprocessed control ears of corn, whereupon the following results were obtained:

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	Brix (°)	
	Corn of this invention	Control corn
Immediately after harvesting	18.0	18.0
After 1 day	17.2	12.8
After 4 days	11.0	3.6
After 5 days	8.6	3.2

	Weight loss (%)	
	Corn of this invention	Control corn
After 1 day	3.6	5.8
After 2 days	7.2	9.6
After 3 days	12.5	15.7
After 4 days	14.0	19.6
After 5 days	17.8	24.2

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The above results indicate that the corn processed according to this invention underwent less variation in degrees brix and weight loss than the control corn and that the effect of preservation of the process is good.

Example 10.

The following recipe was used to prepare a suspension of carnauba wax by the procedure set forth in Example 1.

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	Parts by weight
carnauba wax	10
polyvinyl alcohol	3
sodium oleate	0.8
(or sucrose fatty acid ester	1)
water	100

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The grain size of the particles in the suspension thus prepared was 5 microns with both emulsifiers.

In this suspension, grapefruits were immersed for 1 to 2 seconds and were then dried in a stream of air to form a coating membrane covering the outer surfaces of the grape-

fruits. The grapefruits were then stored at room temperature for 60 days and compared with control grapefruits without surface processing but stored under the same conditions with respect to citric acid content, degrees brix, and loss in weight. The results were as follows:

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Weight loss:

Days lapsed	Grapefruits of the invention	Control grapefruits
15	2.3%	5.1%
30	4.2%	9.3%
60	10.1%	16.9%

Degrees Brix and Citric acid:

Days lapsed	Grapefruits of the invention		Control grapefruits	
	Brix (°)	Acid (%)	Brix (°)	Acid (%)
0	7.9	0.96	7.9	0.96
30	7.8	0.94	7.7	0.90
60	7.8	0.93	7.6	0.86

As is indicated by the above results, the grapefruits processed in accordance with this invention exhibited better results than the control grapefruits with respect to citric acid content, degrees brix and weight loss. Furthermore, the grapefruit processed according to the invention did not show any change in sarcocarp hardness during storage for 90 days but, in contrast, the control grapefruits exhibited severe wilting after storage for 20 days.

Example 11.

A beeswax suspension with a particle size of approximately 2 microns was prepared using the following recipe by an ordinary procedure:

First liquid—	Parts by weight
beeswax	10
sodium oleate	0.8
(or sucrose fatty acid ester	1)
water	80

A second liquid was prepared with the following recipe:

Second liquid—	Parts by weight
acacia (gum arabic)	2
salt (NaCl)	0.4
water	20

First, the acacia was added to the water and dissolved under heating. After complete dissolution of the acacia, the salt was added to

the resulting solution to produce the second liquid.

In the use of these liquids, 22.4 parts by weight of the second liquid were added to 92 parts by weight of the first liquid, and the resulting mixture was made homogeneous by thorough agitation.

In the liquid thus prepared, "Unshū" mandarin oranges (*Citrus Unshū*) were immersed and the coating were then dried in a stream of air. The oranges thus coated were stored in a storage warehouse.

As a result of inspection of these oranges after 3 months, it was found that the decrease in their weight was approximately one-half of that of unprocessed oranges, similar to Example 1, and that, as a result of the salting effect of the salt added in a quantity of approximately 30 percent to the membrane on the surface of the oranges, the number of instances of decay was very small as indicated below.

Decaying (%) after 3 months	
Processed oranges	2.6%
Unprocessed oranges	15.2%

It was found further that a liquid prepared by blending the above-defined first and second liquids from the beginning to form a single liquid coagulated on the third day after preparation because of break-down of the dispersion due to the fact that salt (NaCl) is an electrolyte, but a combination prepared as two separate liquids in the state of a "kit" withstood long-period storage and then, when the two liquids were mixed at the time of use, pro-



duced a liquid which amply retained its dispersion state during the work period.

WHAT WE CLAIM IS:—

- 5 1. A composition for the preservation processing of agricultural products which carry on living functions after harvesting selected from the group consisting of fruits, vegetables, eggs and grains, comprising a dispersion of microparticles as a dispersoid of a hydrophobic substance selected from the group consisting of natural waxes, vegetable fatty oils, hydrogenated fatty oils and mineral oils in an aqueous solution as a dispersion medium of a water-soluble high polymer and a dispersing agent, said water-soluble high polymer being selected from the group consisting of polysaccharides, polysaccharide derivatives, proteins, alginates, and polyvinyl alcohols, in said composition the weight ratio of said hydrophobic substance and said water-soluble high polymer being from 10:0.2 to 10:3; the composition being capable of application as a coating layer to cover the outer surface of an agricultural product and of being dried to form a coating membrane comprising the microparticles dispersed in a matrix of the membrane of the water-soluble high polymer which has been in aqueous solution and having fine continuous microvoids formed between the microparticles and the matrix, the membrane controllably suppressing the respiration of the agricultural product.
- 20 2. A composition as claimed in claim 1, in which the difference between the solubility parameters of the water-soluble high polymer substance and the hydrophobic substance is in the range of from 3 to 15.
- 25 3. A composition as claimed in claim 1 or 2, in which the microparticles have a particle size of from 0.1 micron to 10 microns.
- 30 4. A composition as claimed in any of claims 1 to 3 in which the dispersing agent is an edible material or a material harmless to the human body when absorbed thereby.
- 35 5. A process for preservation of agricultural products which carry on living functions after harvesting selected from the group consisting of fruits, vegetables, eggs and grains, which comprises applying a dispersion as a coating layer to cover the outer surface of an agricultural product, the dispersion being prepared by dispersing a hydrophobic substance selected from the group consisting of natural waxes, vegetable fatty oils, hydrogenated fatty oils and mineral oils in the form of microparticles in an aqueous solution of a water-soluble high polymer and a dispersing agent constituting a dispersion medium; said water-soluble high polymer being selected from the group consisting of polysaccharides, polysaccharide derivatives, proteins, alginates, and polyvinyl alcohols, in said composition the weight ratio of said hydrophobic substance and said water-

soluble high polymer being from 10:0.2 to 10:3; and drying the dispersion thus applied to form a coating membrane comprising the microparticles dispersed in a matrix of the membrane of the water-soluble high polymer which has been in the aqueous solution and having fine continuous microvoids formed between the microparticles and the matrix, thereby controllably to suppress the respiration of the agricultural product.

6. A process as claimed in claim 5, in which the difference between the solubility parameters of the water-soluble high polymer substance and the hydrophobic substance is from 3 to 15.

7. A process as claimed in claim 5 or 6, in which the microparticles have a particle size of from 0.1 micron to 10 microns.

8. A preservation processed agricultural product which comprises: (a) an agricultural product which carries on living functions after harvesting selected from the group consisting of fruits, vegetables, eggs and grains, and (b) a membrane covering the outer surface of the agricultural product, and comprising a water-soluble high polymer substance constituting a matrix and microparticles of a hydrophobic substance dispersed in the matrix; the hydrophobic substance being selected from the group consisting of natural waxes, vegetable fatty oils, hydrogenated fatty oils and mineral oils, and the water-soluble high polymer being selected from the group consisting of polysaccharides, polysaccharide derivatives, proteins, alginates, and polyvinyl alcohols; in said membrane the weight ratio of said hydrophobic substance and said water-soluble high polymer being from 10:0.2 to 10:3; the membrane having fine continuous microvoids between the matrix and the microparticles and thereby controllably suppressing the respiration of the agricultural product itself.

9. A preservation-processed agricultural product as claimed in claim 8, in which the difference between the solubility parameters of the water-soluble high polymer substance the hydrophobic substance is from 3 to 15.

10. A preservation-processed agricultural product as claimed in claim 8 or 9, in which the membrane has a thickness of from 3 to 100 microns, and the dispersed microparticles have a particle size of from 0.1 micron to 10 microns.

11. A composition according to claim 1, substantially as herein described with reference to any of the specific examples.

12. A process according to claim 5, substantially as herein described with reference to the accompanying drawing and/or any of the specific examples.

13. A preservation-processed agricultural product according to claim 8 substantially as herein described with reference to the accompanying drawing and/or any of the specific examples.

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duced a liquid which amply retained its dispersion state during the work period.

WHAT WE CLAIM IS:—

1. A composition for the preservation processing of agricultural products which carry on living functions after harvesting selected from the group consisting of fruits, vegetables, eggs and grains, comprising a dispersion of microparticles as a dispersoid of a hydrophobic substance selected from the group consisting of natural waxes, vegetable fatty oils, hydrogenated fatty oils and mineral oils in an aqueous solution as a dispersion medium of a water-soluble high polymer and a dispersing agent, said water-soluble high polymer being selected from the group consisting of polysaccharides, polysaccharide derivatives, proteins, alginates, and polyvinyl alcohols, in said composition the weight ratio of said hydrophobic substance and said water-soluble high polymer being from 10:0.2 to 10:3; the composition being capable of application as a coating layer to cover the outer surface of an agricultural product and of being dried to form a coating membrane comprising the microparticles dispersed in a matrix of the membrane of the water-soluble high polymer which has been in aqueous solution and having fine continuous microvoids formed between the microparticles and the matrix, the membrane controllably suppressing the respiration of the agricultural product.
2. A composition as claimed in claim 1, in which the difference between the solubility parameters of the water-soluble high polymer substance and the hydrophobic substance is in the range of from 3 to 15.
3. A composition as claimed in claim 1 or 2, in which the microparticles have a particle size of from 0.1 micron to 10 microns.
4. A composition as claimed in any of claims 1 to 3 in which the dispersing agent is an edible material or a material harmless to the human body when absorbed thereby.
5. A process for preservation of agricultural products which carry on living functions after harvesting selected from the group consisting of fruits, vegetables, eggs and grains, which comprises applying a dispersion as a coating layer to cover the outer surface of an agricultural product, the dispersion being prepared by dispersing a hydrophobic substance selected from the group consisting of natural waxes, vegetable fatty oils, hydrogenated fatty oils and mineral oils in the form of microparticles in an aqueous solution of a water-soluble high polymer and a dispersing agent constituting a dispersion medium; said water-soluble high polymer being selected from the group consisting of polysaccharides, polysaccharide derivatives, proteins, alginates, and polyvinyl alcohols, in said composition the weight ratio of said hydrophobic substance and said water-

soluble high polymer being from 10:0.2 to 10:3; and drying the dispersion thus applied to form a coating membrane comprising the microparticles dispersed in a matrix of the membrane of the water-soluble high polymer which has been in the aqueous solution and having fine continuous microvoids formed between the microparticles and the matrix, thereby controllably to suppress the respiration of the agricultural product.

6. A process as claimed in claim 5, in which the difference between the solubility parameters of the water-soluble high polymer substance and the hydrophobic substance is from 3 to 15.

7. A process as claimed in claim 5 or 6, in which the microparticles have a particle size of from 0.1 micron to 10 microns.

8. A preservation processed agricultural product which comprises: (a) an agricultural product which carries on living functions after harvesting selected from the group consisting of fruits, vegetables, eggs and grains, and (b) a membrane covering the outer surface of the agricultural product, and comprising a water-soluble high polymer substance constituting a matrix and microparticles of a hydrophobic substance dispersed in the matrix; the hydrophobic substance being selected from the group consisting of natural waxes, vegetable fatty oils, hydrogenated fatty oils and mineral oils, and the water-soluble high polymer being selected from the group consisting of polysaccharides, polysaccharide derivatives, proteins, alginates, and polyvinyl alcohols; in said membrane the weight ratio of said hydrophobic substance and said water-soluble high polymer being from 10:0.2 to 10:3; the membrane having fine continuous microvoids between the matrix and the microparticles and thereby controllably suppressing the respiration of the agricultural product itself.

9. A preservation-processed agricultural product as claimed in claim 8, in which the difference between the solubility parameters of the water-soluble high polymer substance the hydrophobic substance is from 3 to 15.

10. A preservation-processed agricultural product as claimed in claim 8 or 9, in which the membrane has a thickness of from 3 to 100 microns, and the dispersed microparticles have a particle size of from 0.1 micron to 10 microns.

11. A composition according to claim 1, substantially as herein described with reference to any of the specific examples.

12. A process according to claim 5, substantially as herein described with reference to the accompanying drawing and/or any of the specific examples.

13. A preservation-processed agricultural product according to claim 8 substantially as herein described with reference to the accompanying drawing and/or any of the specific examples.



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