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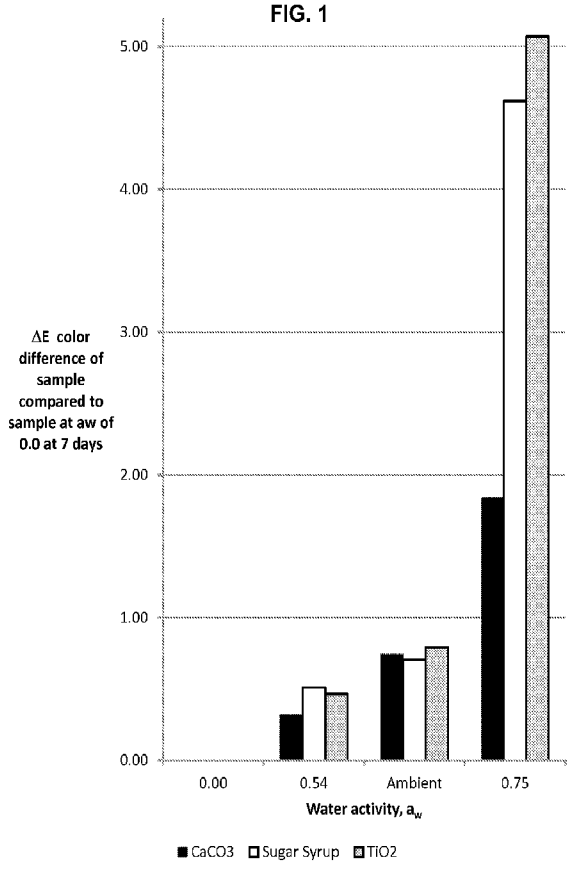
(54) Title: STABILIZATION OF NATURAL BLUE ANTHOCYANIN-CONTAINING COLORANTS AND PRODUCTS MADE

FIG. 1



(57) Abstract: The present invention is directed to a hard panned coating comprising a natural blue anthocyanin-containing colorant, a hard panned confection coated with the same, and a method of hard pan coating an edible product center with the coating such that the color provided by the natural blue anthocyanin-containing colorant to the coating is stabilized.

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STABILIZATION OF NATURAL BLUE ANTHOCYANIN-CONTAINING COLORANTS AND PRODUCTS MADE

BACKGROUND OF THE INVENTION

FIELD

[0001] The present invention relates to a hard panned coating, a hard panned confection coated with the same, and a method of stabilizing the color provided by natural blue anthocyanin-containing colorants in the hard panned coating of the confection.

Description of the Related Art

[0002] There is increasing interest in the food industry to replace synthetic materials for coloring foods with natural colorants.

[0003] One challenge in replacing synthetic colorants with natural colorants in the coating of hard panned confections has been in obtaining the stability of color characteristics provided by synthetic colorants.

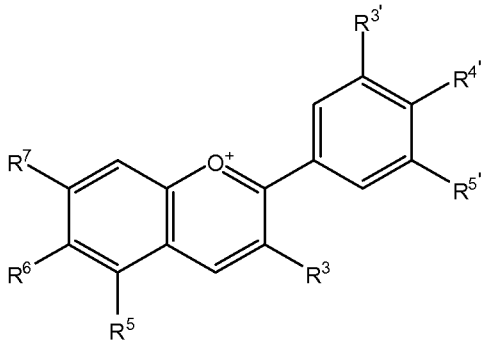
[0004] Natural blue anthocyanin-containing colorants that provide the stability of color characteristics in hard panned confection coatings that is provided by synthetic blue colorants, e.g., FD&C Blue No. 1 and FD&C Blue No. 2, have not been found to this time. The lack of stable natural blue anthocyanin-containing colorants has also made it challenging to obtain desired stable natural green anthocyanin-containing colorants from the blending of natural blue anthocyanin-containing colorants and natural yellow colorants. Red cabbage and purple sweet potato extracts are examples of commercially available natural anthocyanin-containing colorants that may provide blue hues under certain conditions, but these materials do not provide the stability of blue color characteristics in hard panned confection coatings that is provided by synthetic blue colorants such as FD&C Blue No. 1 and FD&C Blue No. 2.

[0005] Anthocyanins are water-soluble compounds widely found in the cell vacuoles of fruits, vegetables, and flower petals, and sometimes, roots, leaves, stems, and bracts of plants. Anthocyanin-containing juices and extracts of these plant materials have been used as natural, edible colorants and to produce colorant compositions, in particular, natural red, purple, and blue hue colorant compositions.

[0006] An anthocyanin comprises an anthocyanidin (the aglycone) esterified to one or more sugar molecules (the glycone(s)) to form a glycoside. Sugar molecules may be attached at the C-3, C-5, C-7, C-3', C-4', and/or C-5' positions. Examples of sugar molecules found in anthocyanin structures are arabinose, galactose, glucose, rhamnose, rutinose, sambubiose, sophorose, and xylose.

[0007] Anthocyanins may also be acylated, i.e., they may have one or more molecules esterified to the sugar molecules, typically at the 6-position of a monosaccharide, but also potentially at the 2-, 3-, or 4-positions. The most common acyl units include those derived from coumaric, ferulic, caffeic, sinapic, gallic, malonic, acetic, malic, succinic, vanillic, and oxalic acids.

[0008] The structure of an anthocyanidin is shown below in the flavylium cation form, which is the primary form under acidic conditions. The anthocyanidin may be substituted with hydrogen, hydroxyl, and/or methoxyl groups at various positions:



wherein R^3 is H or OH,

R^5 is H, OH, or OCH_3,

R^6 is H or OH,

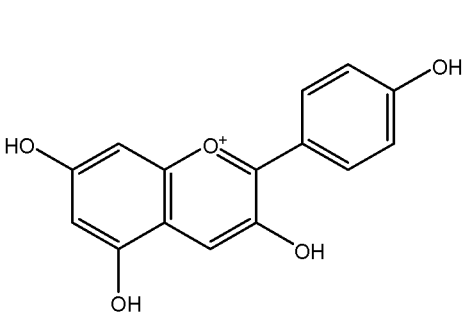
R^7 is OH or OCH_3,

$R^{3'}$ is H, OH, or OCH_3,

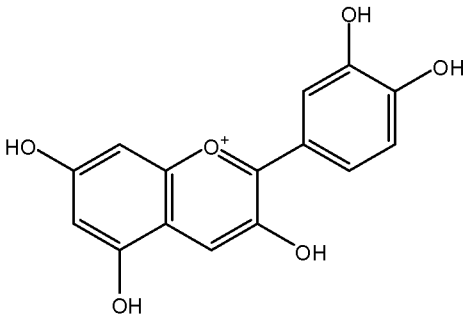
$R^{4'}$ is OH or OCH_3, and

$R^{5'}$ is H, OH, or OCH_3.

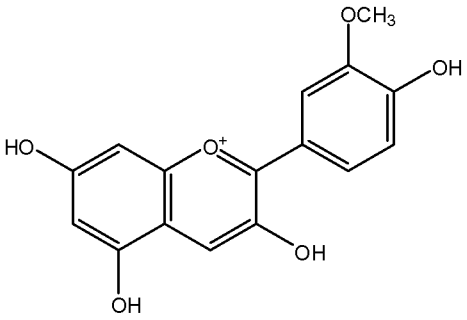
[0009] The most common anthocyanidins in nature are shown by the following structures:



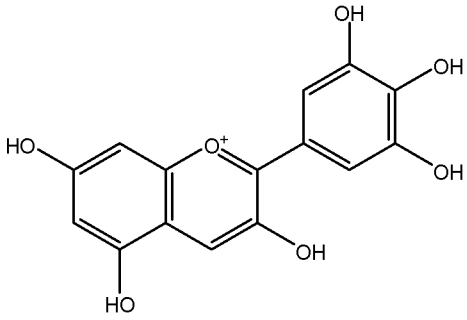
Pelargonidin



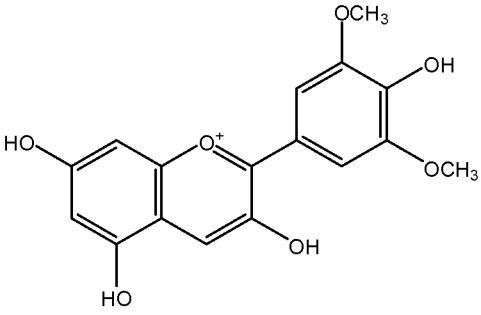
Cyanidin



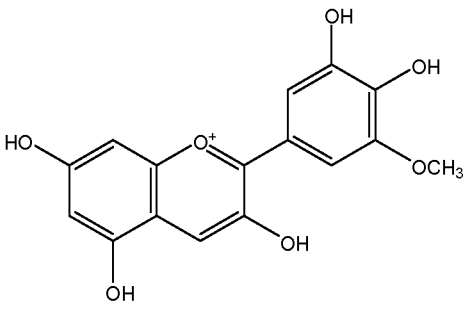
Peonidin



Delphinidin



Malvidin



Petunidin

[0010] Therefore, the class of compounds known as anthocyanins encompasses an enormous number of structurally diverse compounds based on differences in primary structure, glycosylation and acylation patterns.

[0011] Known plant sources of anthocyanins include: (1) vegetables such as red cabbage, purple sweet potato, red potato, blue potato, red radish, black carrot, purple carrot, purple corn, red corn, red onion, purple broccoli, red broccoli, purple cauliflower, rhubarb, black bean, red leaf lettuce, black rice, and eggplant; (2) fruits such as strawberry, raspberry, cranberry, lingonberry, red grape, apple, black currant, red currant, cherry, blueberry, elderberry, bilberry, crowberry, blackberry, chokeberry, gooseberry, açaí, nectarine, peach, plum, blood orange, and blue tomato; and (3) flower petals such as those of 'Heavenly Blue' Morning Glory and 'Better Times' Rose. Each anthocyanin source contains different

amounts of multiple, distinct anthocyanin species, with 15 to 30 structurally distinct anthocyanin molecules being common for a given plant source.

[0012] The color characteristics of anthocyanin-containing juices and extracts of plant materials change as a result of changing pH. Anthocyanin-containing juices and extracts generally exhibit red hues at low pH, and the hue shifts to purple as the pH is increased. Only a few juices and extracts exhibit a blue hue as pH is increased further.

[0013] The change in color of anthocyanin-containing juices and extracts resulting from changes in pH is related to the numerous secondary structures of anthocyanins that may exist in equilibrium with the primary flavylium cation structure in aqueous solution. When pH is changed, the relative quantities of the different equilibrium structures will change. At a given pH, one or more structural forms may predominate, while others are present in low quantities or not present. For example, at very low pH, the flavylium cation form predominates. As pH is increased, molecules in the flavylium cation form may be deprotonated and converted to the carbinol pseudobase form, which may be further converted through loss of a water molecule and a proton to the neutral and ionized quinonoidal base forms, respectively, and further, to the chalcone form. These transformations reduce the quantity of molecules in the flavylium cation form and increase the quantities in the other equilibrium forms to different extents. Therefore, the different equilibrium structures exist in different relative quantities at higher pH compared to low pH. Each structural form of anthocyanin may absorb light differently, resulting in a different perceived color, including no color. Therefore, as the pH of the solution is changed, changes in the relative quantities of the different structural forms may result in changes in the color of the solution.

[0014] The flavylium cation and quinonoidal base structures have conjugated bonds connecting all three rings of the anthocyanin molecules. The extensive delocalized pi bonds allow the flavylium cation and quinonoidal base to absorb visible light, resulting in the perceived red hue of the flavylium cation at low pH and the purple or blue hue of the ionized quinonoidal base at a higher pH. In contrast, the carbinol pseudobase and chalcone structures do not have delocalized pi bonds connecting all three rings and are colorless or slightly yellow.

[0015] The substitution pattern of anthocyanins also affects color. For example, it is generally observed that the hue shifts from pink to purple when hydrogen atoms are replaced with hydroxyl groups. Similarly, the number of glycosyl (sugar) units and the

number and type of acyl units are observed to affect color. However, these phenomena are not well understood.

[0016] Additionally, intermolecular and intramolecular interactions also affect anthocyanin color. The same anthocyanin may produce different hues depending on the other molecules present. For example, it is believed that acyl groups on the anthocyanin sugars can fold in and protect the flavylium cation C-2 position from nucleophilic attack. Therefore, this intramolecular interaction prevents formation of the colorless carbinol pseudobase structure. Similarly, it is believed that anthocyanin molecules self-associate, which is evidenced by the fact that a two-fold increase in anthocyanin concentration can cause a 300-fold increase in chroma, and can change the hue and value as well. It is hypothesized that this self-association is similar to intramolecular stacking, and prevents nucleophilic attack and formation of the carbinol pseudobase structure.

[0017] Although it is known that factors such as pH, anthocyanin chemical structure, substituent patterns, inter- and intra-molecular interactions all impact the color observed in anthocyanin-containing juices and extracts of plant materials, it is not well understood how these factors interact to alter color; i.e., the specific cause and effect are not predictable.

[0018] All of these phenomena may impact the color and color stability of hard panned confections having sugar-based coatings colored with natural anthocyanin-containing colorants. It has been observed that a hard panned sugar-based coating colored with a natural blue anthocyanin-containing colorant will quickly shift from a blue hue to a periwinkle or violet hue shortly after production. When a green-colored hard panned sugar-based coating is prepared using a natural blue anthocyanin-containing colorant in combination with a natural yellow colorant, e.g., turmeric, the color of the coating will quickly shift from a green hue to a mustard hue shortly after production. Factors that may precipitate anthocyanin structural changes and associated color changes in the coatings are believed to include moisture migration out of the coating, moisture ingress into the coating from the environment, metal ions and compounds in water used to prepare sugar syrups, and changes in the crystalline structure of the coating that continue after production has been completed.

[0019] WO 2011/065977 discloses a method of preparing and stabilizing a blue colorant by combining a buffer, an anthocyanin, and a divalent ion source, such as calcium carbonate. In an example, calcium carbonate is intimately combined with a sodium carbonate buffer, red cabbage powder (anthocyanin source), and other ingredients using a high-speed blade

mixer, and the resulting colorant formulation is used for pan coating placebos. There is no contemplation of segregating the calcium carbonate from the anthocyanin material in separate coating layers of the panned coating.

[0020] The prior art has not provided a method of stabilizing the color provided by natural blue anthocyanin-containing colorants in the coating of a hard panned confection without modifying and combining the anthocyanin-containing colorant with other materials. In addition, the prior art has not described hard panned confections having sugar-based coatings colored with natural blue anthocyanin-containing colorants that demonstrate improved color stability closer to the color stability obtained with synthetic blue colorants such as FD&C Blue No. 1 and FD&C Blue No. 2.

[0021] It is desirable to have a method that allows a broad palette of colorants to be used for coloring hard panned coatings for hard panned confections, including natural anthocyanin-containing colorants sourced from juices and extracts of plant materials. In particular, there is a need for a method of stabilizing natural blue anthocyanin-containing colorants in the coating of a hard panned confection. Naturally colored hard panned confections with stable blue and green hues are a desired product of such a method.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] **Fig. 1** demonstrates the effect of no additive, titanium dioxide as an additive, and calcium carbonate as an additive in a first coating syrup on the color stability of hard panned confections colored with a natural blue anthocyanin-containing colorant and stored under different environmental conditions. The figure shows ΔE color difference values for each trial sample after seven days of storage under different environmental conditions compared to the same sample stored at a water activity of 0.0.

[0023] **Fig. 2** demonstrates the effect of titanium dioxide, calcium carbonate, or titanium dioxide and calcium carbonate together as an additive in a first coating syrup on the color stability of hard panned confections colored with an alternate natural blue anthocyanin-containing colorant and stored under different environmental conditions. The figure shows ΔE color difference values for each trial sample after seven days of storage under different environmental conditions compared to the same sample stored at a water activity of 0.0.

[0024] **Fig. 3** demonstrates the effect of using deionized water versus tap water with calcium carbonate as an additive in a first coating syrup on the color stability of hard panned confections colored with a natural blue anthocyanin-containing colorant and stored

under different environmental conditions. The figure shows ΔE color difference values for each trial sample after seven days of storage under different environmental conditions compared to the same sample stored at a water activity of 0.0.

SUMMARY OF THE INVENTION

[0025] The present invention is directed to a hard panned coating comprising a natural blue anthocyanin-containing colorant, wherein the color provided to the coating by the colorant is stabilized.

[0026] In one embodiment, the hard panned coating has a plurality of coating layers, the plurality of coating layers comprising a first coating layer comprising a sugar and a food-grade calcium carbonate and a second coating layer comprising a sugar and a natural blue anthocyanin-containing colorant, wherein none of the plurality of coating layers contains both a natural blue anthocyanin-containing colorant and a food-grade calcium carbonate. In some embodiments, the second coating layer of the hard panned coating also includes a natural yellow colorant.

[0027] In another embodiment, the hard panned coating has a color having a ΔE color difference of 10 or less after seven days of storage at a water activity of 0.75 compared to the color after seven days of storage at a water activity of 0.0. In some embodiments, the hard panned coating has a blue or green color at least partly provided by the natural blue anthocyanin-containing colorant, which has a blue color in aqueous solution at a pH of about 6 to about 10.

[0028] The present invention is also directed to a hard panned confection coated with a hard panned coating comprising a natural blue anthocyanin-containing colorant, wherein the color provided by the colorant to the coating is stabilized.

[0029] In one embodiment, the hard panned confection comprises an edible product center, a hard panned coating having a plurality of coating layers, the plurality of coating layers comprising a first coating layer comprising a sugar and a food-grade calcium carbonate and a second coating layer comprising a sugar and a natural blue anthocyanin-containing colorant, wherein none of the plurality of coating layers contains both a natural blue anthocyanin-containing colorant and a food-grade calcium carbonate. In some embodiments, the second coating layer of the hard panned confection also includes a natural yellow colorant.

[0030] In another embodiment, the hard panned confection has a color having a ΔE color difference of 10 or less after seven days of storage at a water activity of 0.75 compared to the color after seven days of storage at a water activity of 0.0. In some embodiments, the hard panned confection has a blue or green color at least partly provided by the natural blue anthocyanin-containing colorant, which has a blue color in aqueous solution at a pH of about 6 to about 10.

[0031] In another aspect, the present invention is directed to a method of hard pan coating an edible product center with a coating comprising a natural blue anthocyanin-containing colorant, wherein the color provided to the coating by the colorant is stabilized.

[0032] In one embodiment, the method of hard pan coating the edible product center comprises the steps of applying a plurality of coating layers to the edible product center, wherein applying comprises applying a first coating layer comprising a sugar and a food-grade calcium carbonate to the edible product center and applying a second coating layer comprising a sugar and a natural blue anthocyanin-containing colorant to the edible product center, wherein none of the plurality of coating layers contains both a natural blue anthocyanin-containing colorant and a food-grade calcium carbonate. In some embodiments, a natural yellow colorant is included in the second coating layer applied.

[0033] In another aspect, the present invention is directed to a method of stabilizing the color provided by a natural blue anthocyanin-containing colorant to a hard panned coating.

[0034] In one embodiment, the method of stabilizing the color provided by a natural blue anthocyanin-containing colorant to a hard panned coating having a plurality of coating layers comprises applying the plurality of coating layers such that none of the plurality of coating layers contains both a natural blue anthocyanin-containing colorant and a food-grade calcium carbonate.

DETAILED DESCRIPTION OF THE INVENTION

[0035] The present specification provides certain definitions and methods to better define the present invention and to guide those of ordinary skill in the art in the practice of the present invention. Provision, or lack of the provision, of a definition for a particular term or phrase is not meant to imply any particular importance, or lack thereof. Rather, and unless otherwise noted, terms are to be understood according to conventional usage by those of ordinary skill in the relevant art. The terms “first,” “second,” and the like, as used herein,

do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. Also, the terms "a" and "an" do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item.

[0036] The term, "edible," means that which can be eaten by humans and animals as food, and should be distinguished from "non-toxic," which means that which may be ingested and tolerated, but which is not consumed as food.

[0037] A "sugar syrup" is a liquid material comprising at least a sugar and water, wherein the sugar is dissolved in the water in an amount of at least 60% sugar solids by weight of the syrup. Other components may also be present.

[0038] A "coating layer" is a layer obtained by one application of a coating material, e.g., a sugar syrup, to a substrate being coated.

[0039] A "coating" is the total amount of coating material, e.g., one or more sugar syrups, applied to a substrate upon completion of a coating process, which may comprise one or more steps of applying a coating material to the substrate.

[0040] A "divalent metal cation" is a metal atom having a +2 charge, e.g., Ca^{2+}, Mg^{2+}, Cu^{2+}, Fe^{2+}, and the like.

[0041] A "monovalent metal cation" is a metal atom having a +1 charge, e.g., Na^{+}, K^{+}, and the like.

[0042] A "carbonate ion" is an anion having the empirical formula, CO_3^{2-}.

[0043] "Calcium carbonate" is an ionic compound having the empirical formula, $CaCO_3$, and is classified as a carbonate mineral.

[0044] A "food-grade calcium carbonate" is a calcium carbonate material that is of a grade acceptable for use in edible products, e.g., affirmed GRAS (Generally Recognized as Safe) by the U.S. Food and Drug Administration. The food-grade calcium carbonate may be a precipitated calcium carbonate.

[0045] A "colorant" is any substance that imparts color by absorbing or scattering light at different wavelengths. A "natural colorant" is a colorant that exists in or is produced by nature or is sourced therefrom. A "blue colorant" is a colorant that reflects light at wavelengths in the region of 450-495 nanometers and has a maximum UV/VIS wavelength absorbance ranging from 615 to 635 nanometers. A "natural anthocyanin-containing colorant" is a natural colorant comprising anthocyanins sourced from plants. The term, "food-grade," when used herein to describe any colorant, means that the colorant is of a grade acceptable for use in edible products.

[0046] References to "FD&C Blue No. 1" include the different names given to the identical synthetic blue colorant, Brilliant Blue FCF and European Commission E133.

[0047] References to "FD&C Blue No. 2" include the different names given to the identical synthetic blue colorant, Indigo Carmine, Indigotine, or European Commission E132.

[0048] "Hue" refers to the color property that gives a color its name, for example red, orange-red, blue, violet, etc.

[0049] "Chroma" is a color property indicating the purity of a color, where higher chroma is associated with greater purity of hue and less dilution by white, gray, or black.

[0050] "Value" is a color property indicating the lightness or darkness of a color, where higher value is associated with greater lightness.

[0051] The terms "color" and "color characteristics" are used interchangeably, and encompass color properties such as hue, chroma, purity, saturation, intensity, vividness, value, lightness, brightness, and darkness, and color model system parameters used to describe these properties, such as Commission Internationale de l'Eclairage CIE 1976 CIELAB color space L*a*b* values and CIELCH color space L*C*h° values. The CIELAB and CIELCH color models provide more perceptually uniform color spaces than earlier color models. Colorants are analyzed with a spectrophotometer, and CIELAB L*a*b* and CIELCH L*C*h° values are calculated from the spectral data. The L*a*b* and L*C*h° values provide a means of representing color characteristics and assessing the magnitude of difference between two colors.

[0052] L*a*b* values consist of a set of coordinate values defined in a three-dimensional Cartesian coordinate system. L* is the value, or lightness, coordinate. L* provides a scale of lightness from black (0 L* units) to white (100 L* units) on a vertical axis. a* and b* are coordinates related to both hue and chroma. a* provides a scale for greenness (- a* units) to redness (+ a* units), with neutral at the center point (0 a* units), on a horizontal axis. b* provides a scale for blueness (- b* units) to yellowness (+ b* units), with neutral at the center point (0 b* units), on a second horizontal axis perpendicular to the first horizontal axis. The three axes cross where L* has a value of 50 and a* and b* are both zero.

[0053] L*C*h° values consist of a set of coordinate values defined in a three-dimensional cylindrical coordinate system. L* is the value, or lightness, coordinate. L* provides a scale of lightness from black (0 L* units) to white (100 L* units) on a longitudinal axis. h° is the hue coordinate. h° is specified as an angle from 0° to 360° moving counterclockwise around the L* axis. Pure red has a hue angle of 0°, pure yellow has a hue angle of 90°, pure

green has a hue angle of 180°, and pure blue has a hue angle of 270°. The C* coordinate represents chroma and is specified as a radial distance from the L* axis. C* provides a scale from achromatic, i.e., neutral white, gray, or black, at the L* axis (0 C* units) to greater purity of hue as the coordinate moves away from the L* axis (up to 100 or more C* units). C* and h° can be calculated from a* and b* using Equations 1 and 2:

$$C^* = (a^{*2} + b^{*2})^{0.5} \quad (1)$$

$$h^\circ = \arctan\left(\frac{b^*}{a^*}\right) \quad (2)$$

[0054] "Delta E," "ΔE_{ab}*," or "ΔE" is a measure of the magnitude of total color difference between two colors represented in CIELAB L*a*b* color space. It has been reported that an experienced color observer cannot distinguish any difference between two colors when the ΔE is about 2.3 or less. The ΔE of two different colors with L*a*b* values, $L^*_1a^*_1b^*_1$ and $L^*_2a^*_2b^*_2$, is calculated using Equation 3:

$$\Delta E_{ab}^* = \sqrt{(L^*_1 - L^*_2)^2 + (a^*_1 - a^*_2)^2 + (b^*_1 - b^*_2)^2} \quad (3)$$

The CIELAB L*a*b* and CIELCH L*C*h° values of hard panned confections presented herein, in all instances unless stated otherwise, were calculated from spectral data obtained with a Konica Minolta Spectrophotometer CM-3500d operated in reflectance mode, with CIE Standard Illuminant D65 and 10° observer angle.

[0055] The present invention is directed to a hard panned coating comprising a natural blue anthocyanin-containing colorant, wherein the color provided by the colorant to the coating is stabilized. Hard panned coatings are used to provide flavor, texture, and color to edible products, including hard panned confections such as sugar shelled chocolate centers. In the confectionery market, color is a particularly appreciated attribute. Although synthetic colorants have been employed to color confections for a number of years, alternatives are yet desired that would be perceived by consumers as being more naturally derived.

[0056] However, it has been difficult to obtain the color stability provided by synthetic colorants when natural colorants are used in many confectionery product applications. Natural colorants are generally more sensitive to heat, light, moisture, and other environmental factors than synthetic colorants. These factors may cause them to degrade or undergo reactions or transformations that alter their molecular structure. Anthocyanin-containing colorants, for example, will undergo changes in structure with changes in pH, and these changes may alter their perceived color, even rendering them colorless.

[0057] Blue anthocyanin-containing colorants are particularly problematic, as the blue hue that they provide has been observed to be unstable and subject to color shift. When a natural blue anthocyanin-containing colorant is used to color a hard panned coating, the coating color quickly shifts after production from blue to periwinkle or violet. This phenomenon also impacts green colored hard panned coatings colored with a blend of a natural blue anthocyanin-containing colorant and a natural yellow colorant. In these cases, the initial color of the coating quickly shifts from green to mustard colored. Therefore, a solution for stabilizing the color of a natural blue anthocyanin-containing colorant in a hard panned coating is desired.

[0058] In one embodiment of the invention, the hard panned coating has a plurality of coating layers, the plurality of coating layers comprising a first coating layer comprising a sugar and a food-grade calcium carbonate and a second coating layer comprising a sugar and a natural blue anthocyanin-containing colorant, wherein none of the plurality of coating layers contains both a natural blue anthocyanin-containing colorant and a food-grade calcium carbonate. In some embodiments, the second coating layer of the hard panned coating also includes a natural yellow colorant.

[0059] The hard panned coating of the invention comprises at least a first coating layer and a second coating layer, each comprising at least one sugar. The one or more sugars in the first coating layer may be the same or different than the one or more sugars in the second coating layer. The sugars are selected according to their well known properties, e.g., crystallizing ability and flavor impact, to function effectively in a hard pan coating process and deliver the desired organoleptic characteristics to the coating, e.g., crunch and sweetness.

[0060] In embodiments, the sugars are selected from a monosaccharide, a disaccharide, and combinations thereof. In embodiments including a monosaccharide, the sugar is a monosaccharide selected from fructose, glucose, dextrose, maltose, and combinations thereof. In embodiments including a disaccharide, the sugar is sucrose.

[0061] The sugars are preferably provided to the first and second coating layers as sugar syrups comprising one or more sugars and water. The sugar syrups may contain at least 60 wt% sugar solids, or at least 65 wt% sugar solids, or at least 70 wt% sugar solids. The sugar syrups may contain less than 85 wt% sugar solids, or less than 80 wt% sugar solids. In some embodiments, the sugar syrup contains from 70 wt% to 80 wt% sugar solids. In embodiments using sucrose as the sole sugar in a sugar syrup, the sucrose sugar syrup may

be at least 60° Brix, or at least 65° Brix, or at least 70° Brix. The sucrose sugar syrup may be less than 85° Brix, or less than 80° Brix. In some of these embodiments, the sucrose sugar syrup is from 70° Brix to 80° Brix.

[0062] A sugar syrup may also include other components conventionally used in hard panned coatings. Many such components are known in the art and include, but are not limited to, sugar alcohols, high intensity sweeteners, natural polymers, flavors, flavor modifiers, sensates, gums, vitamins, minerals, nutraceuticals, or combinations of these. For example, a gum may be included in a sugar syrup to act as a plasticizer in the crystallized sugar coating.

[0063] At least one sugar syrup used in a coating layer of the hard panned coating comprises one or more natural food-grade colorants. The natural food-grade colorants may be provided in any form, e.g., liquid, crystal, paste, or powder, that dissolves or disperses readily in a sugar syrup for best results in producing the hard panned coating,. Suitable concentrations of natural food-grade colorants can range from 0.01 wt% to 20 wt%, or from 0.05 wt % to 15 wt%, or from 0.1 wt% to 10 wt%.

[0064] In a preferred embodiment, a natural blue anthocyanin-containing colorant is one of the one or more natural food-grade colorants in a sugar syrup used in a coating layer of the hard panned coating. In some of these embodiments, both a natural blue anthocyanin-containing colorant and a natural yellow colorant are included in a sugar syrup used in a coating layer of the hard panned coating.

[0065] Natural blue anthocyanin-containing colorants may be sourced from vegetables, fruits, and flower petals. In some embodiments, the natural blue anthocyanin-containing colorant comprises one or more vegetable, fruit, and flower petal juices and extracts. An "anthocyanin-containing vegetable, fruit, or flower petal juice" may be obtained by pressing liquid out of the fruit, vegetable, or flower petals. An "anthocyanin-containing vegetable, fruit, or flower petal extract" may be obtained by washing macerated fruit, vegetables, or flower petals with a solvent (e.g., water, alcohol). Juices and extracts may contain anthocyanins as well as many other naturally occurring compounds, including, for example, carbohydrates, acids, flavonoids, metal ions, phenolic acids, phenolic acid esters, and vitamins. Vegetable, fruit, and flower petal juices or extracts may include processed juices and extracts, including, for example, reconstituted juices and extracts, deodorized juices and extracts, and juices and extracts subjected to other processes for removing specific or broad classes of compounds.

[0066] Any juice or extract that provides blue hues at high pH, e.g., a pH of 6 to 10, or 7 to 9, may be used. In one embodiment, the source of the natural blue anthocyanin-containing colorant used in the hard panned coating of the invention is a vegetable, fruit, or flower petal juice or extract obtained from red cabbage, purple sweet potato, blue potato, purple carrot, black carrot, blue flower petals, or a combination thereof. In some of these embodiments, the natural blue anthocyanin-containing colorant comprises a red cabbage extract or a combination of a red cabbage extract and a purple sweet potato extract.

[0067] The natural blue anthocyanin-containing colorant may consist of only anthocyanins or may also include other plant compounds and/or added materials typically used with colorants to facilitate their use, e.g., liquid carriers including water, alcohol, and glycerin, and solid carriers including maltodextrin, starch, and sugar. The composition may take the form of a solid, e.g., a powder, or a liquid solution, e.g., an aqueous liquid.

[0068] Suitable natural yellow colorants may include, but are not limited to, curcuminoids (e.g., from turmeric), carotenoids (e.g., from saffron and gac), annatto (e.g., from achiote), and combinations thereof. In some embodiments, the natural yellow colorant is derived from turmeric.

[0069] When a colorant is included in one or more sugar syrups used for hard pan coating, the hard panned coating desirably has a visible color provided by the colorant. A hard panned confection comprising an edible product center coated with this same hard panned coating also has a visible color provided by the colorant. In some embodiments, the hard panned coating has a blue color, and a hard panned confection coated with this same hard panned coating has a blue color. The blue color may be provided at least in part by a natural blue anthocyanin-containing colorant incorporated in the coating. In other embodiments, the hard panned coating has a green color, and a hard panned confection coated with this same hard panned coating has a green color. The green color may be provided at least in part by a natural blue anthocyanin-containing colorant and a natural yellow colorant incorporated in the coating.

[0070] At least one sugar syrup used in a coating layer of the hard panned coating comprises a food-grade calcium carbonate. In one embodiment, the food-grade calcium carbonate is a precipitated calcium carbonate. In some embodiments, the median particle size of the food-grade calcium carbonate is 1 micron or less, 0.8 microns or less, or 0.7 microns or less.

[0071] The amount of calcium carbonate to be used is limited only by practicality, e.g., enough should be used so that the desired benefit will be seen, but desirably, no greater amount will be used than that needed to achieve the same. Advantageously, small amounts, e.g., as low as 1 wt%, of calcium carbonate have found to be effective to provide at least some benefit. Amounts of at least 5 wt%, or 4 wt%, or 3 wt%, or 2 wt%, or 1 wt% are suitable. Amounts of more than 11 wt%, or 12 wt%, or 13 wt%, or 14 wt% or 15 wt% may provide no further benefit, and so, are not used in some embodiments. In some embodiments, the calcium carbonate is provided in the sugar syrup in amounts of from 1 wt% to 15 wt%, or from 3 wt% to 14 wt%, or from 5 wt% to 13 wt% or from 7 wt% to 12 wt%, or from 9 wt% to 10 wt%. In some embodiments, the calcium carbonate is provided in the sugar syrup in amounts of from 1 wt% to 10 wt%.

[0072] Calcium carbonate is preferably included in one or more coating layers of the hard panned coating that do not comprise a colorant, in particular, a natural blue anthocyanin-containing colorant. That is, calcium carbonate is excluded from coating layers that comprise a natural blue anthocyanin-containing colorant, because the alkalinity of calcium carbonate raises pH to about 9 and shifts the color provided by the anthocyanin-containing colorant to turquoise instead of blue. In a preferred embodiment, a sugar and a food-grade calcium carbonate are included in a first coating layer of a hard panned coating, and the first coating layer does not include a natural blue anthocyanin-containing colorant.

[0073] Conversely, a natural blue anthocyanin-containing colorant is preferably included in one or more coating layers of the hard panned coating that do not comprise calcium carbonate. That is, the natural blue anthocyanin-containing colorant is excluded from coating layers that comprise calcium carbonate. In a preferred embodiment, a sugar and a natural blue anthocyanin-containing colorant are included in a second coating layer of a hard panned coating.

[0074] In one embodiment of the hard panned coating, the color of the hard panned coating has a ΔE color difference of 10 or less after seven days of storage at a water activity of 0.75 compared to the color after seven days of storage at a water activity of 0.0. In some embodiments, the ΔE is 8 or less, or 6 or less, or as low as 4 or less. That is, the color of the hard panned coating demonstrates resistance to color change even under challenging environmental moisture conditions.

[0075] A hard panned coating having a stable color provided by a natural blue anthocyanin-containing colorant is of value for use as a coating for a confection. Therefore,

in another aspect, the present invention is directed to a hard panned confection comprising an edible product center and a hard panned coating having a plurality of coating layers, the plurality of coating layers comprising a first coating layer comprising a sugar and a food-grade calcium carbonate and a second coating layer comprising a sugar and a natural blue anthocyanin-containing colorant, wherein none of the plurality of coating layers contains both a natural blue anthocyanin-containing colorant and a food-grade calcium carbonate.

[0076] The coating layers of the hard panned confection may be applied to any desired edible product center. In some embodiments, the edible product center may comprise a natural center, e.g., a nut, groundnut, nut meat, nut paste, dried or infused fruit piece, or dried fruit paste. Or, the edible product center may comprise a confection, e.g., a boiled sugar syrup, caramel, nougat, taffy, toffee, fondant, chocolate, confectionery coating, or combinations of these. Alternatively, the edible product center may comprise a grain-based item, e.g., a cookie, pretzel, biscuit, wafer, cracker, or other baked, crisped, or puffed material. In some embodiments, the edible product center may comprise a natural center, confection, or grain-based item which is then coated with a confection.

[0077] Prior to the application of one or more sugar syrup layers, the surface of the edible product center may be prepared according to known techniques in the art such as gumming, isolating, and stabilizing. For example, in gumming, layers of a high glucose content syrup containing a gum, gelatin, starch, or dextrin may be applied directly to the edible center alternately with a fine crystalline sugar to fill irregularities and smooth ridges. The smoother surface that is obtained may facilitate even coating and adherence of the later applied sugar syrup layers. Isolating is a process of creating a barrier to lipid, water, or natural sugar migration between the edible center and the sugar syrup layers, and may be effected by applying a film containing gelatin or gum to the center in a process similar to gumming. Stabilizing may be required to strengthen a fragile edible center for subsequent hard pan coating with sugar syrups. A cookie center, for example, may be prevented from crumbling during hard pan coating by first being coated with a melted fat, then isolated with a gum-containing film. Preparation of the surface of the edible core may also be completed with one or more applications of a sucrose sugar syrup.

[0078] In some embodiments, sugar syrups may be applied as coating layers directly to the surface of an edible product center. In other embodiments, sugar syrups may be applied as coating layers to a prepared surface of an edible product center, wherein the surface has been prepared according to a known technique including, but not limited to, gumming,

isolating, and stabilizing. In still other embodiments, sugar syrups may be applied as coating layers to a crystallized sugar syrup layer overlying any number of coating layers overlying the edible product center. As the phrase that follows in quotation marks is used herein, the application of a sugar syrup as a coating layer "to an edible product center" does not necessarily denote that the sugar syrup is applied directly to the edible product center. Rather, a sugar syrup that is applied as a coating layer "to an edible product center" may be applied directly to the surface of the edible product center, or to a prepared surface of an edible product center, or to a crystallized sugar syrup layer overlying any number of coating layers overlying the edible product center, within the meaning of the phrase.

[0079] A hard panned confection having a hard panned coating of the invention demonstrates resistance to color change. That is, in some embodiments, the hard panned confection has a color having a ΔE color difference of 10 or less after seven days of storage at a water activity of 0.75 compared to the color after seven days of storage at a water activity of 0.0. Smaller ΔE values of 8 or less, or 6 or less, or 4 or less may also be seen.

[0080] In another aspect, the present invention is directed to a method of hard pan coating an edible product center comprising applying a plurality of coating layers to the edible product center, wherein applying comprises applying a first coating layer comprising a sugar and a food-grade calcium carbonate to the edible product center and applying a second coating layer comprising a sugar and a natural blue anthocyanin-containing colorant to the edible product center, wherein none of the plurality of coating layers contains both a natural blue anthocyanin-containing colorant and a food-grade calcium carbonate. In some embodiments, a natural yellow colorant is included in the second coating layer applied.

[0081] The material of the first coating layer, i.e., comprising a sugar and a food-grade calcium carbonate, may be applied in as many layers as desired to obtain the benefits of color stabilization described. In some embodiments, the number of layers of the first coating material applied is 3 – 7 layers; in other embodiments, 5 – 9 layers; in yet other embodiments, 7 – 11 layers. The material of the second coating layer, i.e., comprising a sugar and a natural anthocyanin-containing colorant, may similarly be applied in as many layers as desired to obtain a desired finished product color. The blue anthocyanin-containing colored coating layers may be applied overlying the uncolored calcium carbonate-containing layers, and in such embodiments, the number of layers applied may be fewer than 40, or fewer than 30, or fewer than 25, or fewer than 20 colored coating layers overlying the uncolored calcium carbonate-containing layers.

[0082] Once hardened, the panned coating may be expected to have a thickness of no more than 3.0 mm, or no more than 2.5 mm, or no more than 2.0 mm, or no more than 1.5 mm, or no more than 1.0 mm. The hard panned coating may also have a thickness of greater than 0.1 mm or greater than 0.2 mm, or greater than 0.3 mm, or greater than 0.4 mm, or greater than 0.5 mm. In some embodiments, the hard panned coating may have a thickness of from 0.1 mm to 3.0 mm, or from 0.2 mm to 2.5 mm, or from 0.3 mm to 2.0 mm, or from 0.4 mm to 1.5 mm, or from 0.5 mm to 1.0 mm.

[0083] The desired edible product center is coated with the desired sugar syrups as coating layers, in the desired number of layers for each as described above, and according to processes and techniques generally known in the art. Generally speaking, the process for manufacturing hard panned confections comprises the deposition of a plurality of coating layers of the sugar syrups, for example, between 10 and 50 layers total, by a series of syrup application and drying cycles carried out, for example, in a rotating pan. Such processes are described, for example, in "Sugar Confectionery and Chocolate Manufacture, R. Lees and E.B. Jackson, Chemical Publishing Company, February 7, 1975, and "Industrial Chocolate Manufacture and Use," editor, S.T. Beckett, Blackie & Son Ltd., Glasgow, 1988, each hereby incorporated herein by reference in its entirety for any and all purposes.

[0001] Such processes may typically be driven by the equipment utilized to perform them, which can be dry equipment or slurry equipment, both types being commercially available from, e.g., Ets Dumoulin & Cie, Tournan-en Brie, France, KOCO Food Tech, Inc., Phoenix, MD and Loynds International, Ltd., Poulton Le Fylde, England.

[0084] Panning is contrasted herein from film coating, i.e., the coatings are applied by a panning process and not a film coating process. While both are industrial processes for preparing coated edible products, such as confections and pharmaceuticals, they are very different processes that make use of very different coating formulations. Panning and some coating processes are performed in a rotating drum or "pan". Typically, the term "panning" is used with regard to the application of sugar-based coatings, such as, e.g., sucrose or dextrose, to masses of centers to produce coated products. The term "film coating" is used with regard to applying coatings that are not based on sugar to masses of centers, where the coating material typically comprises film forming components, such as a modified cellulose, e.g., hydroxypropyl methylcellulose, that is continuously applied to the centers until the desired coating thickness is achieved. Conventional panned coatings do not comprise film forming components, nor do the panned coatings of the present invention.

[0085] In a hard panning process, multiple applications of a highly concentrated sugar syrup are used to build up the uncolored portion of a sugar coating on an edible product center. This is followed by multiple applications of a concentrated sugar syrup containing colorant. The hard panning process comprises the repetitive application of thin layers of a coating solution or composition onto an intermixed mass of centers, while mixing the mass of centers, and the drying of each layer of coating solution or composition during which the sugar in the coating crystallizes between the applications of layers. In contrast, as the film coating process does not require the crystallization of a sugar coating, film coating is a continuous process, typically comprising the simultaneous application of a coating solution, distribution by mixing, and drying of the coating solution. That is, the film coating sprayers are not turned off during the film coating process, but, instead, are run continuously until the desired film coating is applied. The film coating solutions typically contain less than about 10 wt% solids, as higher concentrations would be too viscous to spray. However, in each process, coating material is built up on the center to form the desired coating.

[0086] If the coating is to be colored, an edible colorant is added to the coating solution in the later stages of the coating process. For a hard panned confectionery, following the application of a number of layers of the uncolored sugar syrup to build up the sugar coating, a number of applications of a sugar syrup comprising a colorant are applied to provide the color coat. The color coat can require 30 or more applications of a colored coating solution to achieve the desired color. This is because the amount of dye that can be solubilized in the sugar solution is relatively low due to the high sugar solids content of the sugar coating solution. As a result, the process of building the shell, including the coloring steps, can take many hours.

[0087] In yet another aspect, the present invention is directed to a method of stabilizing a color provided by a natural blue anthocyanin-containing colorant to a hard panned coating having a plurality of coating layers comprising applying the plurality of coating layers such that none of the plurality of coating layers contains both a natural blue anthocyanin-containing colorant and a food-grade calcium carbonate.

[0088] Specific embodiments of the invention will now be demonstrated by reference to the following examples. It should be understood that these examples are disclosed solely to illustrate the invention and variations within the spirit of the invention are anticipated.

EXAMPLE 1

Effect of First Coating Syrup Additives on Color Stability of Hard Panned Confections Colored with Natural Blue Anthocyanin-Containing Colorant under Different Environmental Conditions

[0089] A sugar-based coating was applied to lentil-shaped chocolate centers by a hard panning process. A 74° Brix sugar (sucrose) syrup was prepared with deionized water. A natural blue anthocyanin-containing colorant ("NBA-1") was prepared by combining 75 grams of a liquid red cabbage extract (San Red RCFU, San-Ei Gen F.F.I. (USA), Inc., New York, NY) with 1 gram of a powdered purple sweet potato extract (CH 1000, Chr. Hansen, Inc., Milwaukee, WI) and adjusting to a pH of 8 with 2 M NaOH. A first coating syrup consisting of the sugar syrup with titanium dioxide added at 2.5 wt% was applied to the centers and dried in 5 layers. A second coating syrup consisting of the sugar syrup with the colorant added at 3.7 wt% was applied to the centers and dried in 17 layers. The colored centers were finished with a coating of a polishing gum followed by a wax.

[0090] The above process was repeated with an alternative first coating syrup consisting of the sugar syrup with calcium carbonate added at 10 wt%. The process was again repeated with another alternative first coating syrup consisting of the sugar syrup alone. The second coating syrup and finishing coats were the same for the second and third trials as for the first trial.

[0091] Confectionery pieces from each of the three trials were placed in controlled environments at water activities of 0.0, 0.54, and 0.75, and in an indoor environment under ambient conditions. At seven days, color measurements were performed and L*a*b* values calculated and averaged for 10 confectionery pieces from each storage condition of each trial, as shown in Table 1:

TABLE 1

Sample Name	L*	a*	b*	ΔE compared to sample with same additive at $a_w = 0.0$
NBA-1, TiO_2, $a_w = 0.0$	39.05	2.7	-22.95	---
NBA-1, TiO_2, $a_w = 0.54$	38.61	2.85	-22.98	0.47
NBA-1, TiO_2 Ambient	39.05	3.49	-22.89	0.79
NBA-1, TiO_2, $a_w = 0.75$	39.59	7.74	-22.82	5.07
NBA-1, $CaCO_3$, $a_w = 0.0$	36.89	-1.78	-20.50	---
NBA-1, $CaCO_3$, $a_w = 0.54$	36.71	-1.52	-20.45	0.32
NBA-1, $CaCO_3$, Ambient	37.44	-1.28	-20.47	0.74
NBA-1, $CaCO_3$, $a_w = 0.75$	37.18	-2.39	-18.79	1.84
NBA-1, Sugar Syrup, $a_w = 0.0$	35.74	4.77	-21.92	---
NBA-1, Sugar Syrup, $a_w = 0.54$	35.68	5.20	-22.19	0.51
NBA-1, Sugar Syrup, Ambient	35.84	5.47	-21.89	0.71
NBA-1, Sugar Syrup, $a_w = 0.75$	36.64	8.81	-19.87	4.62

[0092] Figure 1 shows ΔE color difference values for each trial sample at each environmental condition compared to the same sample at a water activity of 0.0. Each sample experienced a color shift at the higher water activities and at ambient condition, with the greatest shift indicated by the largest ΔE values occurring at a water activity of 0.75. The ΔE values for the trial samples having titanium dioxide as an additive and no additive in a first coating layer at a water activity of 0.75 were 5.07 and 4.62, respectively, and indicate a noticeable color shift in the samples. The trial sample having calcium carbonate as an additive in a first coating layer had the least color shift at a water activity of 0.75, as measured by the smallest ΔE value of 1.84. The ΔE value of 1.84 suggests that the color of the calcium carbonate-containing sample at a water activity of 0.75 would be indistinguishable from the color of the same sample at a water activity of 0.0, and this was confirmed by visual observation.

EXAMPLE 2

Effect of First Coating Syrup Additives on Color Stability of Hard Panned Confections Colored with Alternate Natural Blue Anthocyanin-Containing Colorant under Different Environmental Conditions

[0093] A sugar-based coating was applied to lentil-shaped chocolate centers by a hard panning process. A 74° Brix sugar syrup was prepared with deionized water. The colorant used was a natural blue anthocyanin-containing colorant ("NBA-2") consisting of a powdered purple sweet potato and purple carrot extract (CH 5000, Chr. Hansen, Inc., Milwaukee, WI). A first coating syrup consisting of the sugar syrup with titanium dioxide added at 2.5 wt% was applied to the centers and dried in 5 layers. A second coating syrup consisting of the sugar syrup with the colorant added at 0.5 wt% was applied to the centers and dried in 17 layers. The colored centers were finished with a coating of a polishing gum followed by a wax.

[0094] The above process was repeated with an alternative first coating syrup consisting of the sugar syrup with calcium carbonate added at 10 wt%. The process was again repeated with another alternative first coating syrup consisting of the sugar syrup with 5 wt% calcium carbonate and 1.25 wt% titanium dioxide added. The second coating syrup and finishing coats were the same for the second and third trials as for the first trial.

[0095] Confectionery pieces from each of the three trials were placed in controlled environments at water activities of 0.0, 0.54, and 0.75, and in an indoor environment under ambient conditions. At seven days, color measurements were performed and L*a*b* values calculated and averaged for 10 confectionery pieces from each storage condition of each trial, as shown in Table 2:

TABLE 2

Sample Name	L*	a*	b*	ΔE compared to sample with same additive at a_w = 0.0
NBA-2, TiO_2, a_w = 0.0	41.69	-1.09	-20.13	---
NBA-2, TiO_2, a_w = 0.54	40.16	0.48	-20.67	2.26
NBA-2, TiO_2, Ambient	40.97	0.55	-20.52	1.83
NBA-2, TiO_2, a_w = 0.75	42.31	2.29	-19.29	3.54
NBA-2, $CaCO_3$, a_w = 0.0	38.80	-2.33	-18.12	---
NBA-2, $CaCO_3$, a_w = 0.54	38.51	-2.09	-18.2	0.38
NBA-2, $CaCO_3$, Ambient	37.87	-1.20	-18.4	1.49
NBA-2, $CaCO_3$, a_w = 0.75	39.55	-1.56	-16.09	2.30
NBA-2, TiO_2/$CaCO_3$, aw = 0.0	41.32	-0.6	-20.32	---
NBA-2, TiO_2/$CaCO_3$, aw = 0.54	40.49	-0.96	-19.9	1.00
NBA-2, TiO_2/$CaCO_3$, Ambient	40.78	-0.23	-19.94	0.76
NBA-2, TiO_2/$CaCO_3$, aw = 0.75	44.32	-2.15	-16.65	4.99

[0096] Figure 2 shows ΔE color difference values for each trial sample at each environmental condition compared to the same sample at a water activity of 0.0. Each sample experienced a color shift at the higher water activities and at ambient condition, with the greatest shift indicated by the largest ΔE values occurring at a water activity of 0.75. The ΔE values for the trial samples having titanium dioxide and titanium dioxide and calcium carbonate together as an additive in a first coating layer at a water activity of 0.75 were 3.54 and 4.99, respectively, and indicate a noticeable color shift in the samples. The trial sample having calcium carbonate as an additive in a first coating layer had the least color shift at a water activity of 0.75, as measured by the smallest ΔE value of 2.30. The ΔE value of 2.30 suggests that the color of the calcium carbonate-containing sample at a water activity of 0.75 would be indistinguishable from the color of the same sample at a water activity of 0.0, and this was confirmed by visual observation.

EXAMPLE 3

Effect of Different Metal Salts as First Coating Syrup Additives on Color Stability of Hard Panned Confections Colored with Natural Blue Anthocyanin-Containing Colorant

[0097] An experiment was conducted with different metal salts as first coating syrup additives for producing hard panned confections colored with a natural blue anthocyanin-containing colorant. The objective was to compare the effect of carbonates having monovalent cations versus calcium carbonate having a divalent anion. Whereas calcium carbonate is essentially insoluble in water, sodium carbonate and potassium carbonate are soluble in water. This causes them to impact the pH of the sugar syrup, and thus the color of the anthocyanin-containing colorant in the syrup, and to provide no opacifying to the coating. Therefore, titanium dioxide was used in combination with the alternative carbonates to provide the needed opacity.

[0098] Insoluble calcium sulfate was also tested in combination with titanium dioxide as an alternative to calcium carbonate to assess whether the reason for the effectiveness of calcium carbonate was related to the anthocyanin color being "fixed" by the presence of the calcium ion.

[0099] A sugar-based coating was applied to lentil-shaped chocolate centers by a hard panning process. A 74° Brix sugar syrup was prepared with deionized water. The colorant used was a natural blue anthocyanin-containing colorant ("NBA-2") consisting of a powdered purple sweet potato and purple carrot extract (CH 5000, Chr. Hansen, Inc., Milwaukee, WI). A first coating syrup consisting of the sugar syrup with calcium carbonate added at 10 wt% was applied to the centers and dried in 5 layers. A second coating syrup consisting of the sugar syrup with the colorant added at 0.5 wt% was applied to the centers and dried in 17 layers. The colored centers were finished with a coating of a polishing gum followed by a wax.

[00100] The above process was repeated with an alternative first coating syrup consisting of the sugar syrup with 1 wt% sodium carbonate and 2.5 wt% titanium dioxide added. The process was again repeated with another alternative first coating syrup consisting of the sugar syrup with 1 wt% potassium carbonate and 2.5 wt% titanium dioxide added. The process was again repeated with yet another alternative first coating syrup consisting of the sugar syrup with 1 wt% calcium sulfate and 2.5 wt% titanium dioxide added. The second coating syrup and finishing coats were the same for the second to fourth trials as for the first trial.

[00101] Color measurements were performed and L*a*b* values calculated and averaged for 10 confectionery pieces from each trial, as shown in Table 3:

TABLE 3

Sample Name	L*	a*	b*	ΔE compared to sample with $CaCO_3$ as additive
NBA-2, $CaCO_3$	41.69	-1.09	-20.13	---
NBA-2, Na_2CO_3/TiO_2	37.87	-1.20	-18.40	16.70
NBA-2, K_2CO_3/TiO_2	35.59	-9.78	-4.25	17.82
NBA-2, $CaSO_4/TiO_2$	31.12	-9.55	-4.18	8.96

[00102] Compared to the inventive sample containing calcium carbonate as an additive in a first coating syrup, each of the other samples containing alternative metal salts as an additive gave ΔE color difference values of about 9 or greater, indicating noticeable color differences. That is, the alternative metal salts did not provide the same stabilizing effect as calcium carbonate on the natural blue anthocyanin-containing colorant used in the panned coating. In addition, using sodium carbonate and titanium dioxide together as an additive in a first coating syrup resulted in a panned coating color that was unacceptably two-toned. The test results indicate that the color stabilization provided by calcium carbonate may not be attributed to color "fixing" by the calcium ion or to the presence of divalent cations in solution, since calcium carbonate is insoluble in water.

EXAMPLE 4

Effect of Using Tap Water in Coating Syrups and Calcium Carbonate in First Coating Syrup on Color Stability of Hard Panned Confections Colored with Natural Blue Anthocyanin-Containing Colorant under Different Environmental Conditions

[00103] A sugar-based coating was applied to lentil-shaped chocolate centers by a hard panning process. A 74° Brix sugar syrup was prepared with untreated tap water containing small amounts of metal ions such as calcium, sodium, and magnesium. The colorant used was the same as in Example 1, "NBA-1." A first coating syrup consisting of the sugar syrup with calcium carbonate added at 10 wt% was applied to the centers and dried in 5 layers. A second coating syrup consisting of the sugar syrup with the colorant added at 3.7 wt% was applied to the centers and dried in 17 layers. The colored centers were finished with a coating of a polishing gum followed by a wax.

[00104] Confectionery pieces from the trial were placed in controlled environments at water activities of 0.0, 0.54, and 0.75, and in an indoor environment under ambient conditions. At seven days, color measurements were performed and L*a*b* values calculated and averaged for 10 confectionery pieces from each storage condition, as shown in Table 4, along with the L*a*b* values obtained for the calcium carbonate-containing trial samples of Example 1, which used sugar syrups prepared with deionized water:

TABLE 4

Sample Name	L*	a*	b*	ΔE compared to "Tap"sample at a_w = 0.0
NBA-1, $CaCO_3$, Tap, a_w = 0.0	36.47	-0.61	-22.11	---
NBA-1, $CaCO_3$, Tap, a_w = 0.54	36.55	-0.49	-22.23	0.19
NBA-1, $CaCO_3$, Tap, Ambient	36.33	0.28	-22.16	0.90
NBA-1, $CaCO_3$, Tap, a_w = 0.75	36.91	0.63	-21.30	1.55
				ΔE compared to "DI" sample at a_w = 0.0
NBA-1, $CaCO_3$, DI, a_w = 0.0	36.89	-1.78	-20.50	---
NBA-1, $CaCO_3$, DI, a_w = 0.54	36.71	-1.52	-20.45	0.32
NBA-1, $CaCO_3$, DI, Ambient	37.44	-1.28	-20.47	0.74
NBA-1, $CaCO_3$, DI, a_w = 0.75	37.18	-2.39	-18.79	1.84

[00105] Figure 3 shows ΔE color difference values for each trial sample at each environmental condition compared to the same sample at a water activity of 0.0. Each sample experienced a color shift at the higher water activities and at ambient condition, with the greatest shift indicated by the largest ΔE values occurring at a water activity of 0.75. However, no significant differences were seen between the samples using deionized water versus tap water in the sugar syrup.

[00106] The foregoing description of embodiments of the invention is for illustration only and is not to be deemed limiting of the invention, which is defined by the appended claims.

CLAIMS:

1. A hard panned coating having a plurality of coating layers, the plurality of coating layers comprising:
   a) a first coating layer comprising a sugar and a food-grade calcium carbonate, and
   b) a second coating layer comprising a sugar and a natural blue anthocyanin-containing colorant;
   wherein none of the plurality of coating layers contains both a natural blue anthocyanin-containing colorant and a food-grade calcium carbonate.

2. The hard panned coating of claim 1, wherein the hard panned coating has a color having a ΔE color difference of 10 or less after seven days of storage at a water activity of 0.75 compared to the color after seven days of storage at a water activity of 0.0.

3. The hard panned coating of claim 1, wherein the natural blue anthocyanin-containing colorant has a blue color in aqueous solution at a pH of about 6 to about 10.

4. The hard panned coating of claim 1, wherein the second coating layer further comprises a natural yellow colorant.

5. The hard panned coating of claim 1, wherein the first coating layer sugar is provided in a sugar syrup comprising the first coating layer sugar and water.

6. The hard panned coating of claim 5, wherein the sugar syrup comprises sucrose.

7. The hard panned coating of claim 1, wherein the food-grade calcium carbonate has a median particle size of about 0.6 to about 0.8 microns.

8. A hard panned confection comprising:
   a) an edible product center, and
   b) a hard panned coating having a plurality of coating layers, the plurality of coating layers comprising:
      i. a first coating layer comprising a sugar and a food-grade calcium carbonate, and

ii. a second coating layer comprising a sugar and a natural blue anthocyanin-containing colorant;

wherein none of the plurality of coating layers contains both a natural blue anthocyanin-containing colorant and a food-grade calcium carbonate.

9. The hard panned confection of claim 8, wherein the hard panned confection has a color having a ΔE color difference of 10 or less after seven days of storage at a water activity of 0.75 compared to the color after seven days of storage at a water activity of 0.0.

10. The hard panned confection of claim 8, wherein the natural blue anthocyanin-containing colorant has a blue color in aqueous solution at a pH of about 6 to about 10.

11. The hard panned confection of claim 8, wherein the second layer of coating further comprises a natural yellow colorant.

12. The hard panned confection of claim 8, wherein the first coating layer sugar is provided in a sugar syrup comprising the first coating layer sugar and water.

13. The hard panned confection of claim 12, wherein the sugar syrup comprises sucrose.

14. The hard panned confection of claim 8, wherein the food-grade calcium carbonate has a median particle size of about 0.6 to about 0.8 microns.

15. A method of hard pan coating an edible product center comprising applying a plurality of coating layers to the edible product center, wherein applying comprises:

a) applying a first coating layer comprising a sugar and a food-grade calcium carbonate to the edible product center; and

b) applying a second coating layer comprising a sugar and a natural blue anthocyanin-containing colorant to the edible product center,

wherein none of the plurality of coating layers contains both a natural blue anthocyanin-containing colorant and a food-grade calcium carbonate.

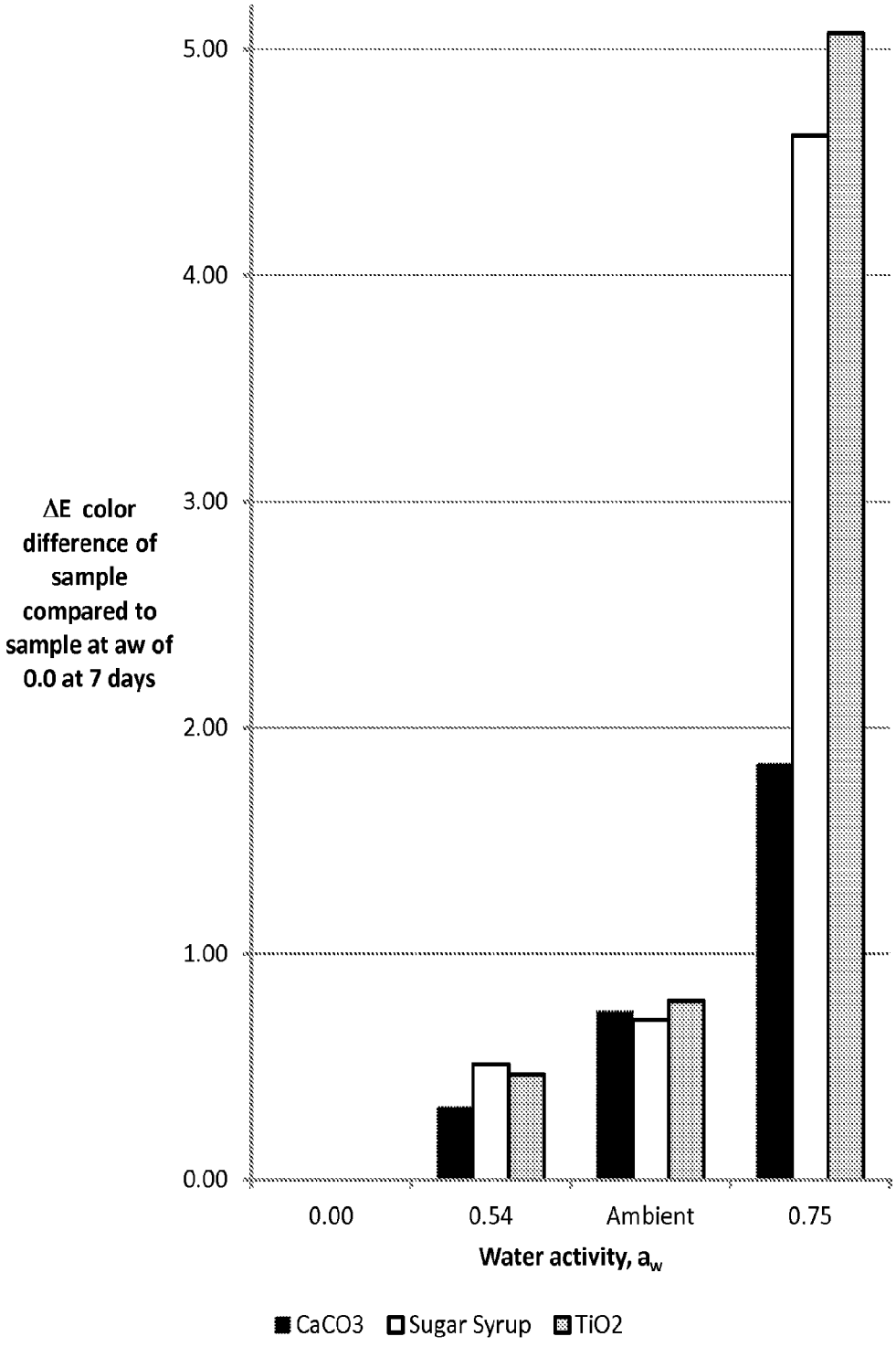
16. The method of claim 15, further comprising at least partially drying the coating layers after each of steps a) and b).

17. The method of claim 15, wherein the first coating layer sugar is provided in a sugar syrup comprising the first coating layer sugar and water.

18. A method of stabilizing a color provided by a natural blue anthocyanin-containing colorant to a hard panned coating having a plurality of coating layers comprising applying the plurality of coating layers such that none of the plurality of coating layers contains both a natural blue anthocyanin-containing colorant and a food-grade calcium carbonate.

1/3

FIG. 1


5.00
4.00
3.00
2.00
1.00
0.00
ΔE color difference of sample compared to sample at aw of 0.0 at 7 days
0.00
0.54
Ambient
0.75
Water activity, a_w
CaCO3
Sugar Syrup
TiO2

2/3

FIG. 2

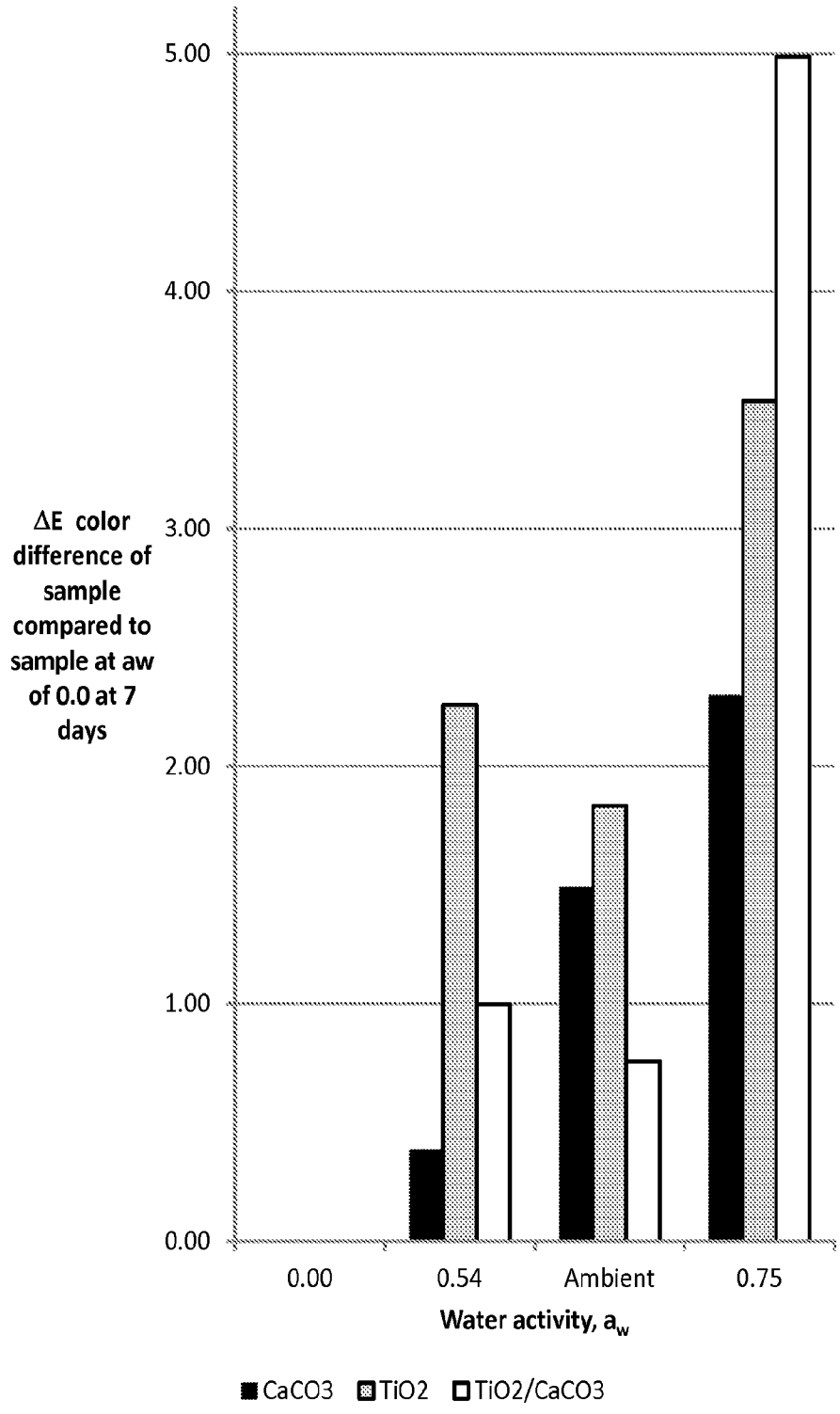
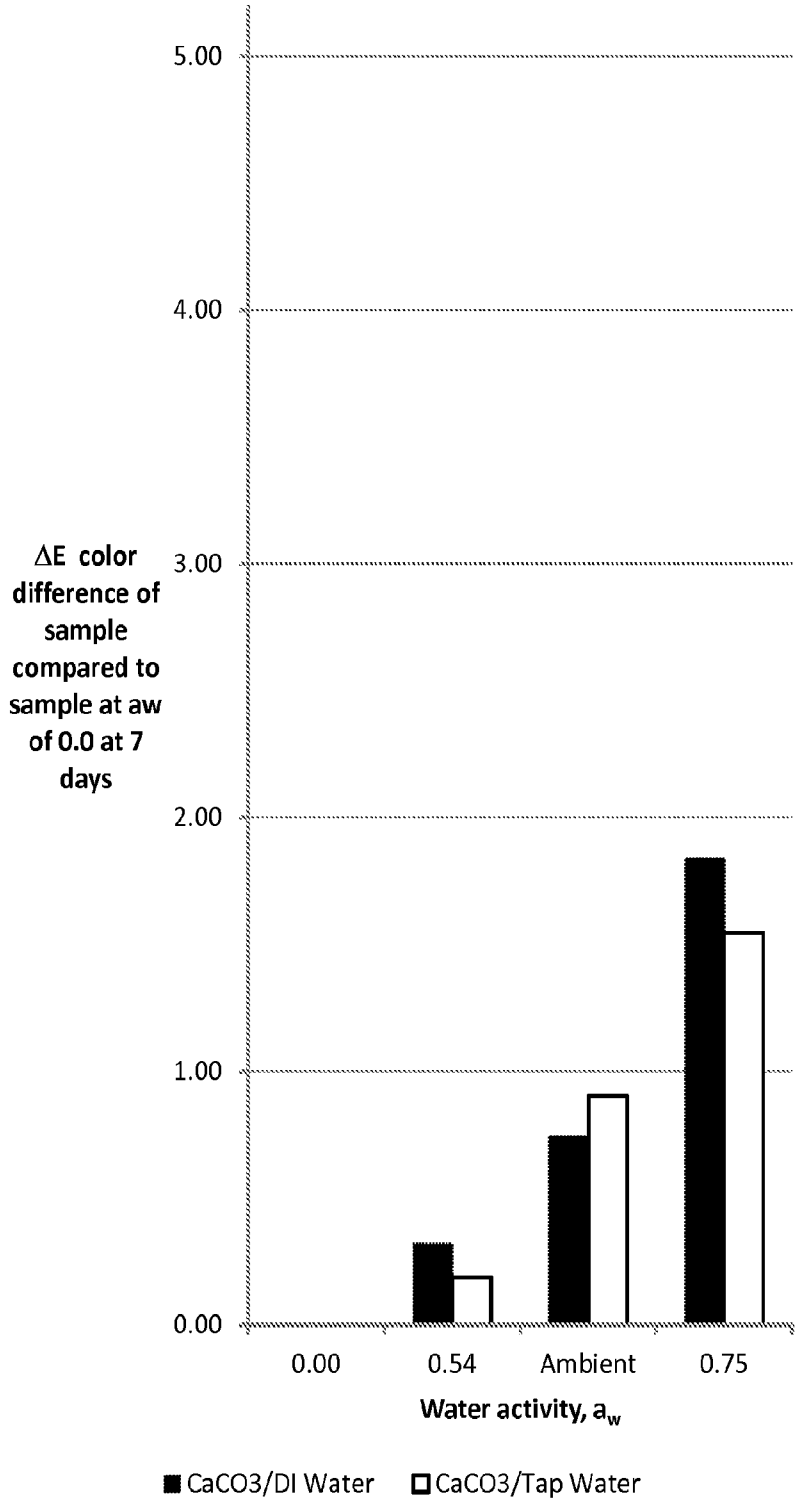

5.00
4.00
3.00
2.00
1.00
0.00
ΔE color difference of sample compared to sample at aw of 0.0 at 7 days
0.00
0.54
Ambient
0.75
Water activity, a_w
CaCO3
TiO2
TiO2/CaCO3

FIG. 3


5.00
4.00
3.00
2.00
1.00
0.00
ΔE color difference of sample compared to sample at aw of 0.0 at 7 days
0.00
0.54
Ambient
0.75
Water activity, a_w
CaCO3/DI Water
CaCO3/Tap Water

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/022649

A. CLASSIFICATION OF SUBJECT MATTER
INV. A23G3/34 A23G3/54
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A23G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, BIOSIS, COMPENDEX, FSTA, IBM-TDB

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/065977 A1 (SENSIENT COLORS INC [US]; MYERS GALE D [US]; JELAVICH MICHAEL C [US];) 3 June 2011 (2011-06-03) cited in the application examples 1-7	1-18
A	EP 2 545 787 A1 (WILD GMBH & CO KG RUDOLF [DE]) 16 January 2013 (2013-01-16) paragraph [0008] - paragraph [0012]; claims 1-5; examples 1-4	1-18
A	US 2004/022904 A1 (NGUYEN ISABELLE [FR]) 5 February 2004 (2004-02-05) examples	1-18
A	EP 1 183 954 A1 (SAN EI GEN FFI INC [JP]) 6 March 2002 (2002-03-06) claims 1-4; figure 1; examples 1,5	1-18

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005/208189 A1 (KURSCHNER KATHLEEN [DE] ET AL) 22 September 2005 (2005-09-22) claims 1-6	1-18

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/022649

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		EP 1515619 A1	23-03-2005
		US 2005208189 A1	22-09-2005
		WO 03105608 A1	24-12-2003

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代理人 冯云 李宓
(51)Int.Cl.
A23G 3/34(2006.01)
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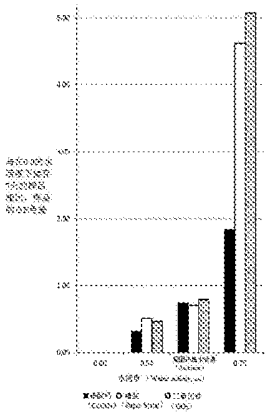
权利要求书2页 说明书18页 附图3页

(54)发明名称

含花青素苷的天然蓝色着色剂的稳定化及制得的产品

(57)摘要

本发明涉及一种包括含花青素苷的天然蓝色着色剂的硬质抛光包衣，用该硬质抛光包衣涂布的硬质抛光糖食，以及用所述包衣对可食用产品的夹心进行硬抛光涂布使得由所述含花青素苷的天然蓝色着色剂提供的颜色稳定化的方法。



CN 105050418 A

1. 一种硬质抛光包衣，所述包衣具有多个包衣层，所述多个包衣层包括：

a) 第一包衣层，所述第一包衣层包括糖和食品级碳酸钙；和

b) 第二包衣层，所述第二包衣层包括糖和含花青素苷的天然蓝色着色剂；

其中所述多个包衣层均不同时包括含花青素苷的天然蓝色着色剂和食品级碳酸钙。

2. 根据权利要求 1 所述的硬质抛光包衣，其中，与在 0.0 的水活度下储存 7 天后的颜色相比，在 0.75 的水活度下储存 7 天后所述硬质抛光包衣具有△ E 色差为 10 或更小的颜色。

3. 根据权利要求 1 所述的硬质抛光包衣，其中，在 pH 为约 6 至约 10 的水性溶液中，所述含花青素苷的天然蓝色着色剂具有蓝色颜色。

4. 根据权利要求 1 所述的硬质抛光包衣，其中，所述第二包衣层进一步包括天然黄色着色剂。

5. 根据权利要求 1 所述的硬质抛光包衣，其中，所述第一包衣层的糖以包括第一包衣层的糖和水的糖浆提供。

6. 根据权利要求 5 所述的硬质抛光包衣，其中，所述糖浆包括蔗糖。

7. 根据权利要求 1 所述的硬质抛光包衣，其中，所述食品级碳酸钙的中值粒径为约 0.6 至约 0.8 微米。

8. 一种硬质抛光糖食，所述糖食包括：

a) 可食用产品的夹心，和

b) 具有多个包衣层的硬质抛光包衣，所述多个包衣层包括：

i. 第一包衣层，所述第一包衣层包括糖和食品级碳酸钙；和

ii. 第二包衣层，所述第二包衣层包括糖和含花青素苷的天然蓝色着色剂；

其中所述多个包衣层均不同时包括含花青素苷的天然蓝色着色剂和食品级碳酸钙。

9. 根据权利要求 8 所述的硬质抛光糖食，其中，与在 0.0 的水活度下储存 7 天后的颜色相比，在 0.75 的水活度下储存 7 天后所述硬质抛光糖食具有△ E 色差为 10 或更小的颜色。

10. 根据权利要求 8 所述的硬质抛光糖食，其中，在 pH 为约 6 至约 10 的水性溶液中，所述含花青素苷的天然蓝色着色剂具有蓝色颜色。

11. 根据权利要求 8 所述的硬质抛光糖食，其中，所述第二包衣层进一步包括天然黄色着色剂。

12. 根据权利要求 8 所述的硬质抛光糖食，其中，所述第一包衣层的糖以包括所述第一包衣层的糖和水的糖浆提供。

13. 根据权利要求 12 所述的硬质抛光糖食，其中，所述糖浆包括蔗糖。

14. 根据权利要求 8 所述的硬质抛光糖食，其中，所述食品级碳酸钙的中值粒径为约 0.6 至约 0.8 微米。

15. 一种对可食用产品的夹心进行硬抛光涂布的方法，所述方法包括将多个包衣层施加至所述可食用产品的夹心，其中，所述施加包括：

a) 将第一包衣层施加至所述可食用产品的夹心，所述第一包衣层包括糖和食品级碳酸钙；和

b) 将第二包衣层施加至所述可食用产品的夹心，所述第二包衣层包括糖和含花青素苷的天然蓝色着色剂；

其中所述多个包衣层均不同时包含括含花青素苷的天然蓝色着色剂和食品级碳酸钙。

16. 根据权利要求 15 所述的方法，所述方法还包括在步骤 a) 和步骤 b) 的每一步之后，至少部分地干燥所述包衣层。

17. 根据权利要求 15 所述的方法，其中，所述第一包衣层的糖以包括第一包衣层的糖和水的糖浆提供。

18. 一种使颜色稳定化的方法，所述颜色由含花青素苷的天然蓝色着色剂提供至具有多个包衣层的硬质抛光包衣，所述方法包括施加多个包衣层，使得所述多个包衣层都不同时含有含花青素苷的天然蓝色着色剂和食品级碳酸钙。

含花青素苷的天然蓝色着色剂的稳定化及制得的产品

技术领域

[0001] 本发明涉及一种硬质抛光包衣，涂有该硬质抛光包衣的硬质抛光糖食，以及使通过在糖食的硬质抛光包衣中含花青素苷的天然蓝色着色剂提供的颜色稳定的方法。

背景技术

[0002] 在食品工业中对用天然着色剂代替合成材料来着色食品的兴趣日益增大。

[0003] 在硬质抛光糖食的包衣中，用天然着色剂代替合成着色剂的一个挑战已经存在于获得合成着色剂提供的颜色特征的稳定性中。

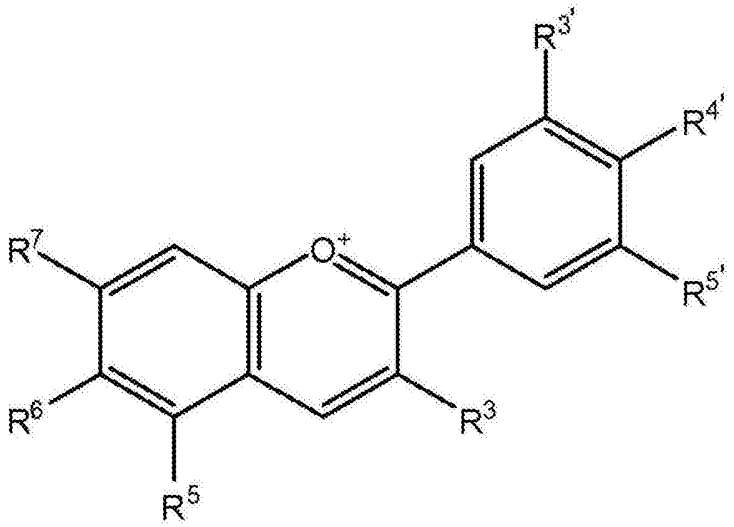
[0004] 到目前为止尚未发现在硬质抛光糖食包衣中提供颜色特征的稳定性的含花青素苷的天然蓝色着色剂，该颜色特征由合成的蓝色着色剂提供，例如美国联邦食品、药品和化妆品法案蓝 1 号 (FD&C Blue No.1) 和美国联邦食品、药品和化妆品法案蓝 2 号 (FD&C Blue No.2)。稳定的含花青素苷的天然蓝色着色剂的缺乏也已使得从含花青素苷的天然蓝色着色剂和天然黄色着色剂的混和物中获得所需的稳定的含花青素苷的天然绿色着色剂成为一种挑战。红球甘蓝和紫甘薯的提取物是在一定条件下可提供蓝色色调的可商购的含花青素苷的天然着色剂的实例，但是这些材料不能提供硬质抛光糖食的包衣中提供的蓝色特征的稳定性，这种稳定性由合成的蓝色着色剂，诸如 FD&C 蓝 1 号和 FD&C 蓝 2 号提供。

[0005] 花青素苷 (anthocyanin) 是在水果、蔬菜和花瓣，以及有时在植物的根、叶、茎和苞片的细胞液泡中发现的水溶性化合物。至少部分地由于其宽泛的可用性，含花青素苷的蔬菜和水果的汁和提取物已经被用作天然可食用着色剂，并用于生产着色剂，特别是天然的红色、紫色和蓝色色调的着色剂。

[0006] 花青素苷 (anthocyanin) 包含与一个或多个糖分子 (糖基 (glycone)) 酯化以形成糖苷的花色素 (anthocyanidin)(糖苷配基 (aglycone))。糖分子可附接至 C-3、C-5、C-7、C-3’、C-4’ 和 / 或 C-5’ 位。在花青素苷结构中发现的糖分子的例子是 :阿拉伯糖、半乳糖、葡萄糖、鼠李糖、芸香糖、接骨木二糖 (sambubiose)、槐糖和木糖。

[0007] 花青素苷还可被酰化，即，它们可具有一个或多个与糖分子酯化的分子，通常位于单糖的 6- 位，但还可能在 2- 位、3- 位或 4- 位。最常见的酰基单元包括来自香豆酸、阿魏酸、咖啡酸、芥子酸、没食子酸、丙二酸、乙酸、苹果酸、琥珀酸、香草酸和草酸的那些酰基单元。

[0008] 花色素 (anthocyanidin) 结构以如下的黄鎓盐 (flavylium) 阳离子形式示出，该形式是酸性条件下的主要形式。花色素可在不同位置被氢、羟基和 / 或甲氧基取代 :



其中，R^3为 H 或 OH；

R^5为 H、OH 或 OCH_3；

R^6为 H 或 OH；

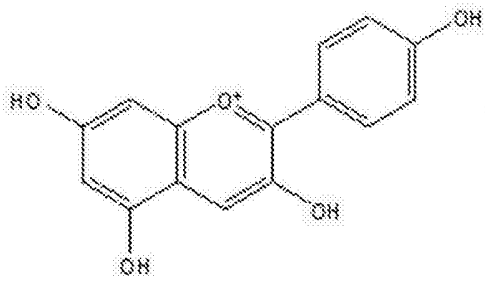
R^7为 OH 或 OCH_3；

$R^{3'}$为 H、OH 或 OCH_3；

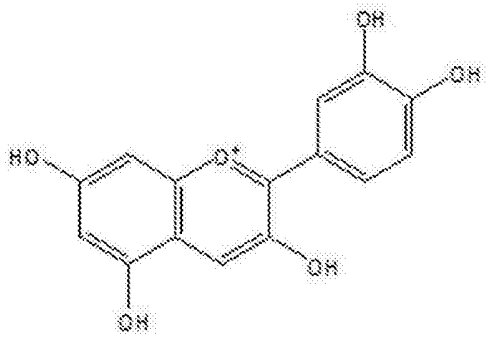
$R^{4'}$为 OH 或 OCH_3；且

$R^{5'}$为 H、OH 或 OCH_3；

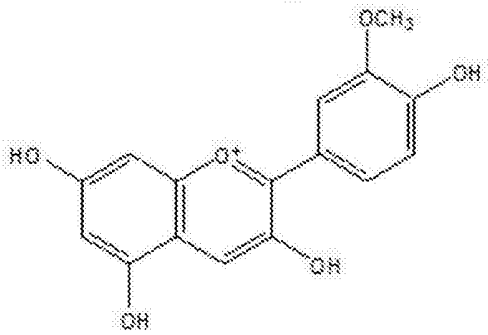
[0009] 以下结构示出了最常见的天然花色素：



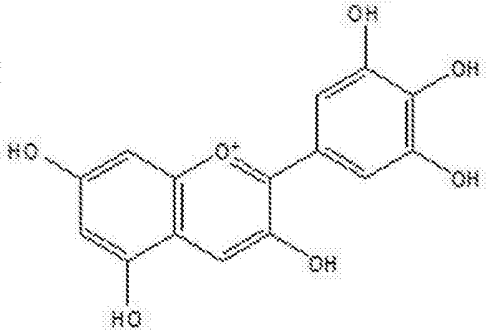
花葵素（Pelargonidin）



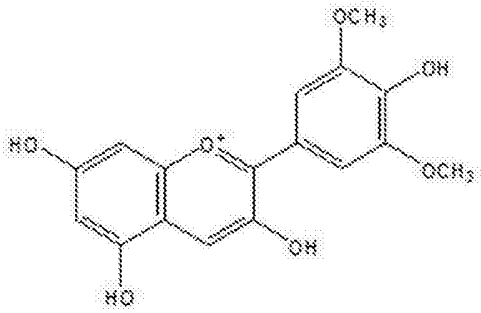
矢车菊色素（Cyanidin）



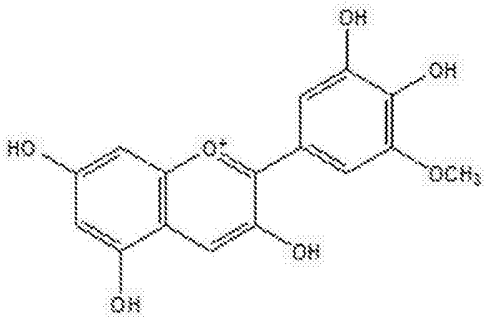
芍药色素（Peonidin）



花翠素（Delphinidin）



锦葵色素（Malvidin）



牵牛花色素（Petunidin）

[0010] 因此，基于主要结构、糖基化和酰化模式的差异，已知为花青素苷的化合物类型涵盖大量的结构多样的化合物。

[0011] 已知的花青素苷的植物来源包括：(1) 蔬菜，例如红球甘蓝、紫甘薯、红马铃薯、蓝马铃薯、红萝卜，黑胡萝卜、紫胡萝卜、紫玉米、红玉米、红洋葱、紫椰菜、红椰菜、紫菜花、大黄、黑豆、红叶莴苣、黑米和茄子；(2) 水果，例如草莓、树莓、蔓越橘、越橘、红葡萄、苹果、黑加仑、红加仑、樱桃、蓝莓、接骨木果、越桔、岩高兰、黑莓、花楸果、醋栗、黑浆果(açaí)、油桃、桃、李、血橙和蓝番茄；以及 (3) 花瓣，例如“天蓝色”的牵牛花和“美好时光”玫瑰的花瓣。每种花青素苷源包含不同含量的多种不同的花青素苷种类，15 至 30 种结构不同的花青素苷分子对于给定植物来源是相同的。

[0012] 植物材料的含花青素苷的汁液和提取物的颜色特征因 pH 变化而变化。含花青素苷的汁液和提取物在低 pH 下通常呈现出红色色调，并且随着 pH 增大该色调迁移至紫色。随着 pH 进一步增大，只有一些汁液和提取物呈现出蓝色色调。

[0013] 由 pH 变化引起的含花青素苷的汁液和提取物的颜色变化与花青素苷的大量次

级结构相关，在水性溶液中这些次级结构与黄鎓盐阳离子主要结构存在平衡。当 pH 变化时，不同平衡结构的相对量将变化。在给定的 pH 下，一种或多种结构形式可占主流，而其他的结构形式以较低的量存在或者不存在。例如，在非常低的 pH 下，黄鎓盐阳离子形式占主流。随着 pH 增大，黄鎓盐阳离子形式中的分子可去质子并转化成甲醇假碱 (carbinol pseudobase) 的形式，该甲醇假碱可分别通过失去水分子和质子进一步转化成中性的和离子化的醌式碱形式 (ionized quinonoidal base form)，并进一步转化成查尔酮形式 (chalcone form)。这些转化减少了黄鎓盐阳离子形式的分子的量，并且不同程度地增加了其它平衡形式的量。因此，与低 pH 相比，在较高的 pH 下，不同的平衡结构以不同的相对量存在。花青素苷的每种结构形式可有差别地吸收光，产生不同的感知的颜色，包括无色。因此，随着溶液 pH 变化，不同结构形式的相对量的变化可导致溶液颜色的变化。

[0014] 黄鎓盐阳离子和醌式碱的结构具有连接花青素苷分子的所有三个环的共轭键。大范围的不定域的 π 键允许黄鎓盐阳离子和醌式碱吸收可见光，导致在低 pH 下产生黄鎓盐阳离子的感知到的红色色调，以及在较高的 pH 下产生离子化的醌式碱的紫色或蓝色色调。相比而言，甲醇假碱和查尔酮结构不具有连接所有三个环的不定域的 π 键，并且为无色或淡黄色。

[0015] 花青素苷的取代方式还影响颜色。例如，通常观察到当氢原子被羟基取代时，色调从粉色迁移至紫色。相似地，观察到糖基（糖）单元的数量和酰基单元的类型影响颜色。然而，尚未彻底理解这些现象。

[0016] 此外，分子间和分子内的相互作用同样影响花青素苷的颜色。根据存在的其它分子，同一种花青素苷可产生不同的色调。例如，人们相信花青素苷糖上的酰基基团可引入，并保护黄鎓盐阳离子 C-2 位不受亲核性攻击。因此，该分子内的相互作用防止形成无色的甲醇假碱结构。相似地，人们相信花青素苷分子自连接 (self-associate)，这由以下事实证实：花青素苷浓度增加两倍可导致色度增加 300 倍，并可改变色调和值。假设该自连接类似于分子内的堆积 (intramolecular stacking)，并防止亲核性攻击以及形成甲醇假碱结构。

[0017] 尽管已知例如 pH、花青素苷化学结构、取代方式、分子间和分子内的相互作用等因素均影响植物材料的含花青素苷的汁液和提取物中观察到的颜色，尚不清楚如何使这些因素相互作用以改变颜色，即特定的起因和影响不可预知。

[0018] 所有这些现象可影响具有糖基包衣的硬质抛光糖食的颜色和颜色稳定性，该糖基包衣用含花青素苷的天然着色剂着色。已经观察到，用含花青素苷的天然蓝色着色剂着色的硬质抛光糖基包衣在生产后不久将快速地从蓝色色调迁移至长春花色调或紫罗兰色调。当使用含花青素苷的天然蓝色着色剂结合天然黄色着色剂，例如姜黄制备绿色的硬质抛光糖基包衣时，包衣的颜色将在生产后不久从绿色色调快速迁移至芥末色调。认为可促进包衣中花青素苷结构变化和相关颜色变化的因素包括湿气迁移出包衣，湿气从环境侵入包衣，用于制备糖浆的水中的金属离子和化合物，以及已经完成制备之后继续的包衣的晶体结构的变化。

[0019] WO 2011/065977 公开了一种通过使缓冲剂、花青素苷和二价离子源，例如碳酸钙结合来制备蓝色着色剂并使其稳定化的方法。在实施例中，使用高速叶片式混合器将碳酸钙与碳酸钠缓冲液、红球甘蓝粉（花青素苷源）以及其它成分紧密地结合，并将所得着色剂配合物用于抛光包衣安慰剂 (placebo)。没有意图将碳酸钙与花青素苷材料在抛光包衣的

单独包衣层中分离。

[0020] 现有技术没有提供在不改变及混合含花青素苷的着色剂和其它材料的情况下，使硬质抛光糖食的包衣中的含花青素苷的天然蓝色着色剂提供的颜色稳定化的方法。此外，现有技术未说明具有用含花青素苷的天然蓝色着色剂着色的糖基包衣的硬质抛光糖食，该含花青素苷的天然蓝色着色剂呈现出改善的颜色稳定性，更接近由合成的蓝色着色剂，例如 FD&C 蓝 1 号和 FD&C 蓝 2 号获得的颜色稳定性。

[0021] 理想的是提供一种方法，使得能将宽色域的着色剂用于使硬质抛光糖食用的硬质抛光包衣着色，该着色剂包括来源于植物材料的汁液和提取物的含花青素苷的天然着色剂。具体地，需要一种使硬质抛光糖食的包衣中的含花青素苷的天然蓝色着色剂稳定化的方法。具有稳定的蓝色和绿色色调的自然着色的硬质抛光糖食是此类方法的理想产品。

附图说明

[0022] 图 1 示出了在第一包衣浆中不含添加剂、含二氧化钛作为添加剂以及含碳酸钙作为添加剂对硬质抛光糖食的颜色稳定性的影响，该糖食用含花青素苷的天然蓝色着色剂着色，并在不同的环境条件下储存。该图示出了在不同环境条件下储存 7 天后每个试验样品与在 0.0 的水活度下储存的同一样品相比的 ΔE 色差值。

[0023] 图 2 示出了在第一包衣浆中含有二氧化钛、碳酸钙、或者二氧化钛和碳酸钙一起作为添加剂对硬质抛光糖食的颜色稳定性的影响，该糖食用含替代的含花青素苷的天然蓝色着色剂着色，并在不同的环境条件下储存。该图示出了在不同环境条件下储存 7 天后每个试验样品与在 0.0 的水活度下储存的同一样品相比的 ΔE 色差值。

[0024] 图 3 示出了在第一包衣浆中使用去离子水相对于自来水与碳酸钙作为添加剂对硬质抛光糖食的颜色稳定性的影响，该糖食用含花青素苷的天然蓝色着色剂着色，并在不同的环境条件下储存。该图示出了在不同环境条件下储存 7 天后每个试验样品与在 0.0 的水活度下储存的同一样品相比的 ΔE 色差值。

发明内容

[0025] 本发明涉及一种硬质抛光包衣，其包括含有蓝色花青素苷的天然着色剂，其中通过所述着色剂提供至包衣的颜色被稳定化。

[0026] 在一个实施方式中，所述硬质抛光包衣具有多个包衣层，所述多个包衣层包括第一糖包层和第二包衣层，所述第一包衣层包括糖和食品级碳酸钙，所述第二包衣层包括糖和含花青素苷的天然蓝色着色剂，其中所述多个包衣层都不同时含有含花青素苷的天然蓝色着色剂和食品级碳酸钙。在一些实施方式中，硬质抛光包衣的第二包衣层还包括天然黄色着色剂。

[0027] 在另一个实施方式中，与在 0.0 的水活度下储存 7 天后的颜色相比，在 0.75 的水活度下储存 7 天后所述硬质抛光包衣具有 ΔE 色差为 10 或更小的颜色。在一些实施方式中，所述硬质抛光包衣具有至少部分由含花青素苷的天然蓝色着色剂提供的蓝色或绿色颜色，在 pH 为约 6 至约 10 的水性溶液中，所述含花青素苷的天然蓝色着色剂具有蓝色颜色。

[0028] 本发明涉及一种具有硬质抛光包衣的硬质抛光糖食，所述硬质抛光包衣含有蓝色花青素苷的天然着色剂，其中通过所述着色剂提供至包衣的颜色被稳定化。

[0029] 在一个实施方式中，所述硬质抛光糖食包括可食用的产品夹心 (center)、具有多个包衣层的硬质抛光包衣，所述多个包衣层包括第一包衣层和第二包衣层，所述第一包衣层包括糖和食品级碳酸钙，所述第二包衣层包括糖和含花青素苷的天然蓝色着色剂，其中所述多个包衣层都不同时含有含花青素苷的天然蓝色着色剂和食品级碳酸钙。在一些实施方式中，硬质抛光糖食的第二包衣层还包括天然黄色着色剂。

[0030] 在另一实施方式中，与在 0.0 的水活度下储存 7 天后的颜色相比，在 0.75 的水活度下储存 7 天后，所述硬质抛光糖食具有 ΔE 色差为 10 或更小的颜色。在一些实施方式中，所述硬质抛光糖食具有至少部分由含花青素苷的天然蓝色着色剂提供的蓝色或绿色颜色，在 pH 为约 6 至约 10 的水性溶液中，所述含花青素苷的天然蓝色着色剂具有蓝色颜色。

[0031] 在另一方面，本发明涉及一种用包衣对可食用产品的夹心进行硬抛光涂布的方法，所述包衣包括含花青素苷的天然蓝色着色剂，其中通过所述着色剂提供至包衣的颜色被稳定化。

[0032] 在一个实施方式中，对可食用产品的夹心进行硬抛光涂布的方法包括以下步骤：将多个包衣层涂覆至可食用产品的夹心，其中涂覆包括向可食用产品的夹心涂覆第一包衣层，和向可食用产品的夹心涂覆第二包衣层，所述第一包衣层包括糖和食品级碳酸钙，所述第二包衣层包括糖和含花青素苷的天然蓝色着色剂，其中所述多个包衣层都不同时含有含花青素苷的天然蓝色着色剂和食品级碳酸钙。在一些实施方式中，在所涂覆的第二包衣层中包括天然黄色着色剂。

[0033] 在另一方面，本发明涉及一种使得由含花青素苷的天然蓝色着色剂提供至硬质抛光包衣的颜色稳定化的方法。

[0034] 在一个实施方式中，使得由含花青素苷的天然蓝色着色剂提供至具有多个包衣层的硬质抛光包衣的颜色稳定化的方法包括涂覆多个包衣层，使得所述多个包衣层都不同时含有含花青素苷的天然蓝色着色剂和食品级碳酸钙。

具体实施方式

[0035] 本说明书提供某些定义和方法，以更好地限定本发明，并指导本领域普通技术人员实施本发明。提供或未提供特定术语或表述的定义不是指暗示任何特殊的重要性或缺乏重要性。相反，除非另作说明，术语应根据相关领域普通技术人员的常规使用来理解。文中所用术语“第一”、“第二”等不指定任何顺序、数量或重要性，而是用于使一个要素与另一个要素区分开。同样，术语“一 (a)”和“一 (an)”不是指数量限定，而是指存在至少一个提及的项目。

[0036] 术语“可食用的”指人类和动物可作为食物食用的，并应能与“无毒的”区分，“无毒的”指可被消化并耐受，但不作为食物食用。

[0037] “糖浆”是至少包括糖和水的液体材料，其中糖以糖浆重量的至少 60％糖固体的量溶解在水中。还可存在其他组分。

[0038] “包衣层”是通过将包衣材料，例如糖浆一次施加 (application) 至被涂布的基材所得到的层。

[0039] “包衣”是在涂布工艺完成期间，涂覆至基材的包衣材料，例如一种或多种糖浆的总量，，该涂布工艺可包括将包衣材料涂覆至基材的一个或多个步骤。

[0040] “二价金属阳离子”是带 +2 电荷的金属原子，例如，Ca^{2+}、Mg^{2+}、Cu^{2+}、Fe^{2+}等。

[0041] “一价金属阳离子”是带 +1 电荷的金属原子，例如，Na^{+}、K^{+}等。

[0042] “碳酸根离子 (carbonate ion)”是具有实验式 CO_3^{2} 的阴离子。

[0043] “碳酸钙”是具有实验式 $CaCO_3$的离子化合物，并被分类为碳酸盐矿物。

[0044] “食品级碳酸钙”是具有对用于可食用产品可接受的级别的碳酸钙材料，例如美国食品药物管理局认证的 GRAS（通常认为是安全的）。食品级碳酸钙可为沉淀的碳酸钙。

[0045] “着色剂”是通过吸收或散射不同波长的光来赋予颜色的任何物质。“天然的着色剂”是天然存在或天然产生的，或者是天然来源的着色剂。“蓝色着色剂”是反射波长在 450-495 纳米区域内的光，并在 615-635 纳米范围内具有最大紫外 / 可见 (UV/VIS) 波长吸收的着色剂。“含花青素苷的天然着色剂”是包括来源于植物的花青素苷的天然着色剂。术语“食品级”，当在文中用于描述任何着色剂时，是指着色剂具有用于可食用产品的可接受的级别。

[0046] 提及的药品和化妆品法案蓝 1 号“FD&C 蓝 1 号”包括对相同的合成的蓝色着色剂给出的不同名称，亮蓝 FCF(Brilliant Blue FCF) 和欧盟委员会 E133(European Commission E133)。

[0047] 提及的“FD&C 蓝 2 号”包括对相同的合成的蓝色着色剂给出的不同名称，靛蓝胭脂红 (Indigo Carmine)、靛蓝 (Indigotine) 或欧盟委员会 E132(European Commission E132)。

[0048] “色调”是指为颜色命名的颜色性质，例如红色、桔红色、蓝色、紫罗兰色等。

[0049] “色度”是指示颜色纯度的颜色性质，其中较高的色度与较高纯度的色调以及较少被白色、灰色或黑色稀释有关。

[0050] “值 (value)”是指示颜色明度或暗度的颜色性质，较高的值与较高的明度有关。

[0051] 术语“颜色”和“颜色特征”可互换使用，并且涵盖颜色性质，例如色调、色度、纯度、饱和度、强度、鲜明度 (vividness)、值、明度、亮度和暗度，以及用于描述这些性质的颜色模型系统的参数，诸如国际照明委员会 CIE 1976 CIELAB 颜色空间的 L*a*b* 值和 CIELCH 颜色空间的 L*C*h° 值。CIELAB 和 CIELCH 颜色模型提供了比更早期的颜色模型视觉上更均匀的颜色空间。用分光光度计分析着色剂，并且由光谱数据计算 CIELAB L*a*b* 值和 CIELCH L*C*h° 值。L*a*b* 值和 L*C*h° 值提供表示颜色特征和评价两种颜色之间差异大小的方法。

[0052] L*a*b* 值由三维笛卡尔坐标系中定义的一组坐标值组成。L* 是值坐标或亮度坐标。L* 提供了竖直轴上从黑色 (0L* 单位）至白色 (100L* 单位）的亮度标度。a* 和 b* 是与色调和色度相关的坐标。a* 提供水平轴上从绿色 (-a* 单位）至红色 (+a* 单位）的标度，中性色位于中心点处 (0a* 单位）。b* 提供第二水平轴上从蓝色 (-b* 单位）至黄色 (+b* 单位）的标度，中性色位于中心处 (0b* 单位），第二水平轴垂直于第一水平轴。在 L* 值为 50 且 a* 和 b* 均为 0 时三个轴相交。

[0053] L*C*h° 值由三维笛圆柱坐标系中定义的一组坐标值组成。L* 值坐标或亮度坐标。L* 提供纵轴上从黑色 (0L* 单位）至白色 (100L* 单位）的亮度标度。h° 是色调坐标。h° 被指定为围绕 L* 轴逆时针反向移动 0° 至 360° 的角度。纯红色具有 0° 的色调角，纯黄色具有 90° 的色调角，纯绿色具有 180° 的色调角，且纯蓝色具有 270° 的色调角。C* 坐标表

示色度，并被指定为距离 L* 轴的径向距离。随着坐标从 L* 轴远移（直至 100 或更多个 C* 单位），C* 提供在 L* 轴（0 个 C* 单位）处从非彩色，即中性的白色、灰色或黑色，至更高纯度的色调。使用方程式 1 和 2 可由 a* 和 b* 计算 C* 和 h° 。

$$C^* = (a^{*2}+b^{*2})^{0.5} \quad (1)$$

$$h^\circ = \arctan\left(\frac{b^*}{a^*}\right) \quad (2)$$

[0054] “德尔塔 E(Delta E)”、“ΔE_{ab}^*”或“ΔE”是国际照明委员会 (Commission Internationale de l'Eclairage,CIE)CIELAB L*a*b* 颜色空间中表示的两种颜色之间总的色差大小的量度。据报道，当 ΔE 为约 2.3 或更小时，有经验的颜色观察师不能区分两种颜色之间的任何差异。用方程式 3 计算 L*a*b* 值为 $L^*_1a^*_1b^*_1$ 和 $L^*_2a^*_2b^*_2$ 的两种不同颜色的 ΔE：

$$\Delta E_{ab}^* = \sqrt{(L^*_1 - L^*_2)^2 + (a^*_1 - a^*_2)^2 + (b^*_1 - b^*_2)^2} \quad (3)$$

在所有情况下，除非另作声明，文中提供的硬质抛光糖食的 CIELAB L*a*b* 值和 CIELCH L*C*h° 值由柯尼卡美能达 (Konica Minolta) 分光光度计 CM-3500d 获得的光谱数据计算，该分光光度计以反射模式，采用 CIE 标准光源 D65 和 10° 的观察角来操作。

[0055] 本发明涉及一种硬质抛光包衣，其包括含有蓝色花青素苷的天然着色剂，其中通过所述着色剂提供至包衣的颜色被稳定化。硬质抛光包衣用于为可食用的产品，包括硬质抛光糖食，如有糖外壳的巧克力夹心提供风味、质地和颜色。在糖食市场中，颜色是特别被认可的属性。尽管多年来已将合成的着色剂用于使糖食着色，但是仍期望被消费者接受的为天然来源的替代物。

[0056] 然而，当在许多糖食产品应用中使用天然着色剂时，一直难以获得合成着色剂所提供的颜色稳定性。天然着色剂通常比合成着色剂对热、光、湿度和其它环境因素更敏感。这些因素可导致它们变质，或者经历改变它们的分子结构的反应或转变。例如，含花青素苷的着色剂随着 pH 变化经历结构的变化，且这些变化可改变它们被感知到的颜色，甚至使它们无色。

[0057] 含蓝色花青素苷的着色剂通常是有问题的，因为它们提供的蓝色色调经观察不稳定，并且经历色移。当含花青素苷的天然蓝色着色剂用于使硬质抛光包衣着色时，包衣的颜色在从蓝色变成长春花色或紫罗兰色之后快速迁移。该现象还影响绿色着色的硬质抛光包衣，该硬质抛光包衣用含花青素苷的天然着色剂和天然黄色着色剂的混合物着色。在这些情况下，包衣的初始颜色快速从绿色迁移至经着色的芥末色。因此，使含花青素苷的天然蓝色着色剂的颜色稳定化的方案是需要的。

[0058] 在本发明的一个实施方式中，硬质抛光包衣具有多个包衣层，所述多个包衣层包括第一包衣层和第二包衣层，所述第一包衣层包括糖和食品级碳酸钙，所述第二包衣层包括糖和含花青素苷的天然蓝色着色剂，其中所述多个包衣层都不同时含有含花青素苷的天然蓝色着色剂和食品级碳酸钙。在一些实施方式中，硬质抛光包衣的第二包衣层还包括天然黄色着色剂。

[0059] 本发明的硬质抛光包衣至少包括第一包衣层和第二包衣层，两个包衣层分别包括至少一种糖。第一包衣层中的一种或多种糖可与第二包衣层中一种或多种糖相同或不同。

根据其熟知的性能选择上述糖，例如结晶化能力和风味效果，以在抛光的硬涂布过程中有效地起作用，并将所需的感官特性传递至包衣，例如嘎吱声和甜味。

[0060] 在实施方式中，上述糖选自单糖、二糖和它们的组合。在包括单糖的实施方式中，糖选自果糖、葡萄糖、右旋糖、麦芽糖和它们的组合。在包括二糖的实施方式中，上述糖是蔗糖。

[0061] 这些糖优选以包括一种或多种糖和水的糖浆被提供至第一包衣层和第二包衣层。该糖浆可包含至少 60wt％糖固体，或者至少 65wt％糖固体，或者至少 70wt％糖固体。上述糖浆可包含少于 85wt％的糖固体，或少于 80wt％的糖固体。在一些实施方式中，糖浆包含 70wt％至 80wt％的糖固体。在使用蔗糖作为糖浆中的唯一的糖的实施方式中，蔗糖糖浆可为至少 60° 白利度 (Brix)，或至少 65° Brix，或者至少 70° Brix。蔗糖糖浆可小于 85° Brix，或小于 80° Brix。在这些实施方式的一些中，蔗糖糖浆为 70° Brix 至 80° Brix。

[0062] 糖浆还可包括常用于硬质抛光包衣的其它组分。许多此类组分在本领域是已知的，包括但并不限于糖醇、高强度的甜味剂、天然的聚合物、香料、香料改性剂、感知剂 (sensate)、树胶、维生素、矿物质、营养物质 (nutraceutical) 或它们的组合。例如，树胶可包括在糖浆中用作结晶的包衣中的增塑剂。

[0063] 硬质抛光包衣的包衣层中所用的至少一种糖浆包括一种或多种天然的食品级着色剂。天然的食品级着色剂可以任何形式提供，例如液体、晶体、膏体或粉末，为了最佳地致使产生硬质抛光包衣，该食品级着色剂易于溶解或分散在糖浆中。天然食品级着色剂的合适浓度范围可为 0.01wt％至 20wt％，或 0.05wt％至 15wt％，或 0.1wt％至 10wt％。

[0064] 在优选实施方式中，含花青素苷的天然蓝色着色剂是硬质抛光包衣的包衣层中所用糖浆中的一种或多种天然食品级着色剂中的一种。在这些实施方式的一些中，硬质抛光包衣的包衣层中所用糖浆中同时包括含花青素苷的天然蓝色着色剂和天然黄色着色剂。

[0065] 含花青素苷的天然蓝色着色剂可来源于蔬菜、水果和花瓣。在一些实施方式中，含花青素苷的天然蓝色着色剂包括一种或多种蔬菜、水果和花瓣的汁液和提取物。“含花青素苷的蔬菜、水果或花瓣的汁液”可通过从水果、蔬菜或花瓣压出液体来获得。“含花青素苷的蔬菜、水果或花瓣的提取物”可通过用溶剂（例如水、乙醇）洗涤浸软的水果、蔬菜或花瓣来获得。汁液和提取物可包含花青素苷以及许多其它天然存在的化合物，包括，例如碳水化合物、酸、类黄酮、金属离子、酚酸、酚酸的酯和维生素。蔬菜、水果和花瓣的汁液或提取物可包括经处理的汁液和提取物，例如包括复原的汁液和提取物、脱臭的汁液和提取物，以及经受用于去除特定类别或宽泛类别的化合物的其它过程的汁液和提取物。

[0066] 可使用在高 pH 下，例如在 pH 为 6 至 10，或 7 至 9 时提供蓝色色调的任何汁液或提取物。在一个实施方式中，本发明的硬质抛光包衣中所用的含花青素苷的天然着色剂的来源为蔬菜、水果或花瓣的汁液，或者从红球甘蓝、紫甘薯、蓝马铃薯、紫胡萝卜、黑胡萝卜、蓝色花瓣获得的提取物，或它们的组合。在这些实施方式的一些中，含花青素苷的天然蓝色着色剂包括红球甘蓝提取物或者红球甘蓝提取物和紫甘薯提取物的组合。

[0067] 含花青素苷的天然蓝色着色剂可仅由花青素苷组成，或者还可包括其它植物化合物和 / 或通常与有利于它们的应用的着色剂一起使用的添加材料，例如包括水、乙醇和甘油的液体载体，以及包括麦芽糖糊精、淀粉和糖的固体载体。上述组合物可采用固体，例如

粉末，液体溶液，例如水性液体的形式。

[0068] 合适的天然黄色着色剂可包括，但不限于姜黄素（例如来自姜黄）、类胡萝卜素（例如来自藏红花和木鳖果 (gac)）、胭脂树橙（例如来自胭脂树）和它们的组合。在一些实施方式中，天然黄色着色剂来源于姜黄。

[0069] 当在用于硬质抛光包衣的一种或多种糖浆中包括着色剂时，该硬质抛光包衣理想地具有由着色剂提供的可见到的颜色。包括用该相同的硬质抛光包衣涂覆的可食用产品夹心的硬质抛光糖食也具有由着色剂提供的可见到的颜色。在一些实施方式中，硬质抛光包衣具有蓝色颜色，且涂覆由该相同硬质抛光包衣的硬质抛光糖食具有蓝色颜色。蓝色颜色可至少部分地由包衣中并入的含花青素苷的天然蓝色着色剂提供。在一些实施方式中，硬质抛光包衣具有绿色颜色，且涂覆由该相同硬质抛光包衣的硬质抛光糖食具有蓝色颜色。绿色颜色可至少部分地由包衣中并入的含花青素苷的天然蓝色着色剂和天然黄色着色剂提供。

[0070] 硬质抛光包衣的包衣层中所用的至少一种糖浆包括食品级碳酸钙。在一个实施方式中，食品级碳酸钙是沉淀的碳酸钙。在一些实施方式中，食品级碳酸钙的中值粒径为 1 微米或更小，0.8 微米或更小，或者 0.7 微米或更小。

[0071] 碳酸钙的用量仅受实用性限制，例如应使用足量，使得将可看出所需效果，但理想地，将使用不大于实现该效果所需量的量。有利地，已经发现少量，例如低至 1wt％的碳酸钙能有效提高至少一些效果。至少 5wt％，或 4wt％，或 3wt％，或 2wt％，或 1wt％的量是合适的。多于 11wt％，或 12wt％，或 13wt％，或 14wt％，或 15wt％的量不再提供更进一步的效果，因此，不用于一些实施方式中。在一些实施方式中，碳酸钙以 1wt％至 15wt％，或 3wt％至 14wt％，或 5wt％至 13wt％，或 7wt％至 12wt％，或 9wt％至 10wt％的量提供于糖浆中。在一些实施方式中，碳酸钙以 1wt％至 10wt％的量提供于糖浆中。

[0072] 碳酸钙优选地被包含在硬质抛光包衣的一个或多个包衣层中，该一个或多个包衣层不包括着色剂，特别是含花青素苷的天然蓝色着色剂。也就是说，碳酸钙被排除于包括含花青素苷的天然蓝色着色剂的包衣层之外，因为碳酸钙的碱性使 pH 升至约 9，并使含花青素苷的着色剂提供的颜色迁移至青绿色，而不是迁移至蓝色。在优选实施方式中，在硬质抛光包衣的第一包衣层中包括糖和食品级碳酸钙，且该第一包衣层不包括含花青素苷的天然蓝色着色剂。

[0073] 相反，含花青素苷的天然蓝色着色剂优选地被包含在硬质抛光包衣的一个或多个包衣层中，该一个或多个包衣层不包括碳酸钙。也就是说，含花青素苷的天然蓝色着色剂被排除于包括碳酸钙的包衣层之外。在优选实施方式中，在硬质抛光包衣的第二包衣层中包括糖和含花青素苷的天然蓝色着色剂。

[0074] 在硬质抛光包衣的一个实施方式中，与在 0.0 的水活度下储存 7 天后的颜色相比，在 0.75 的水活度下储存 7 天后，所述硬质抛光包衣的颜色具有 10 或更小的 ΔE 色差。在一些实施方式中，ΔE 为 8 或更小，或者 6 或更小，或者低至 4 或更小。也就是说，硬质抛光包衣的颜色验证了即使在严苛的环境湿度条件下对抗颜色变化性。

[0075] 具有由含花青素苷的天然蓝色着色剂提供的稳定颜色的硬质抛光包衣具有用作糖食用包衣的价值。因此，在另一个方面中，本发明涉及一种硬质抛光糖食，其包括可食用产品的夹心、具有多个包衣层的硬质抛光包衣，该多个包衣层包括第一包衣层和第二包衣

层，该第一包衣层包括糖和食品级碳酸钙，该第二包衣层包括糖和含花青素苷的天然蓝色着色剂，其中多个包衣层都不同时含有含花青素苷的天然蓝色着色剂和食品级碳酸钙。

[0076] 硬质抛光包衣的包衣层可被涂覆至任何所需的可食用产品夹心。在一些实施方式中，可食用产品夹心可包括天然夹心，例如坚果、花生、坚果仁、坚果酱、干的或浸泡的果块，或者干的水果酱。或者，可食用产品的夹心可包括糖食，例如煮沸的糖浆、焦糖、果仁糖、乳脂糖、太妃糖、软糖、巧克力、糖食的包衣，或者它们的组合。或者，可食用产品的夹心可包括谷物类物质，例如甜饼干、咸饼干、软饼、薄饼、脆饼，或者其它烘焙的、松脆的或蓬松的物质。在一些实施方式中，可食用产品的夹心可包括天然夹心，糖食，或者用糖食涂布的谷物类物质。

[0077] 在涂覆一个或多个糖浆层之前，根据本领域已知的技术，例如涂胶、离析(isolate)和稳定化，可制备可食用产品的夹心的表面。例如，在涂胶时，可将含有树胶、明胶、淀粉或糊精的高葡萄糖含量的糖浆的层直接涂覆至与细晶体的糖交替的可食用的夹心，以填充不规则处和光滑边缘。获得的较光滑的表面可有利于均一的包衣和后续涂覆的糖浆层的附着。离析是在可食用夹心和糖浆层之间产生对脂质、水或天然糖迁移的障壁的过程，并可通过在与涂胶相似的过程中，将含有明胶或树胶的薄膜施加至夹心来实现。稳定化可被要求用于增强用于后续利用涂胶进行硬抛光涂布的易碎的可食用夹心。例如，可防止饼干夹心在通过首先用融化的脂肪涂布，然后用含树胶的膜隔开进行抛光硬涂布期间破裂。制备可食用芯的表面还可用一次或多次涂覆蔗糖糖浆来完成。

[0078] 在一些实施方式中，糖浆可作为包衣层直接涂覆至可食用产品夹心的表面。在其它实施方式中，糖浆可作为包衣层涂覆至所制得的可食用产品夹心的表面，其中该表面已经根据已知的技术制备，该已知技术非限制性包括涂胶、离析和稳定化。在另一些实施方式中，糖浆可作为包衣层涂覆至覆盖任何数量包衣层的结晶的糖浆层，该任何数量的包衣层覆盖可食用产品的夹心。如文中所用引号后的表述，将糖浆作为包衣层涂覆至“可食用产品的夹心”不一定是指糖浆被直接涂覆至可食用产品的夹心。反之，在该表示的含义内，作为包衣涂覆至“可食用产品的夹心”的糖浆可直接涂覆至可食用产品夹心的表面，或者涂覆至所制得的可食用产品夹心表面，或者涂覆至覆盖任何数量的包衣层的结晶糖浆层，该任何数量的包衣层覆盖可食用产品的夹心。

[0079] 具有本发明的硬质抛光包衣的硬质抛光糖食证明耐颜色改变。也就是说，在一些实施方式中，与在0.0的水活度下储存7天后的颜色相比，在0.75的水活度下储存7天后，硬质抛光糖食具有 ΔE 色差为10或更小的颜色。还可看到8或更小，或者6或更小，或者4或更小的较小 ΔE 值。

[0080] 在另一个方面，本发明涉及对可食用产品的夹心进行硬抛光涂布的方法，包括以下步骤：将多个包衣层涂覆至可食用产品的夹心，其中涂覆包括向可食用产品的夹心涂覆第一包衣层，和向可食用产品的夹心涂覆第二包衣层，该第一包衣层包括糖和食品级碳酸钙，该第二包衣层包括糖和含花青素苷的天然蓝色着色剂，其中该多个包衣层都不同时含有含花青素苷的天然蓝色着色剂和食品级碳酸钙。在一些实施方式中，在所涂覆的第二包衣层中包含天然黄色着色剂。

[0081] 第一包衣层的材料，即包括糖和食品级碳酸钙，可以获得所述颜色稳定的效果所需的层数一样多的层涂覆。在一些实施方式中，涂覆的第一包衣材料的层数为3-7层；在其

它实施方式中，为 5-9 层；在另一些实施方式中，为 7-11 层。第二包衣层的材料，即包括糖和含花青素苷的天然着色剂，相似地可以获得成品颜色所需的层数一样多的层涂覆。可涂覆含蓝色花青素苷的着色包衣层，覆盖含碳酸钙的无色层，并且在这些实施方式中，所涂覆的层数可为覆盖含碳酸钙的无色层的少于 40，或者少于 30，或者少于 25，或者少于 20 个着色的包衣层。

[0082] 一旦硬化，抛光的包衣可预期具有不超过 3.0mm，或者不超过 2.5mm，或者不超过 2.0mm，或者不超过 1.5mm，或者不超过 1.0mm 的厚度。硬质抛光包衣还可具有大于 0.1mm，或者大于 0.2mm，或者大于 0.3mm，或者大于 0.4mm，或者大于 0.5mm 的厚度。在一些实施方式中，硬质抛光包衣可具有 0.1mm 至 3.0mm，或者 0.2mm 至 2.5mm，或者 0.3mm 至 2.0mm，或者 0.4mm 至 1.5mm，或者 0.5mm 至 1.0mm 的厚度。

[0083] 以如上文所述的各层的所需层数，并根据本领域公知的方法和技术，用所需的糖浆涂覆所需可食用产品的夹心成为包衣层。总的来说，生产硬质抛光包衣糖食的方法包括通过例如在旋转盘中进行一系列糖浆涂覆和干燥循环来沉积糖浆的多个包衣层，例如一共 10 至 50 个层。例如，在“糖食和巧克力制造”(“Sugar Confectionery and Chocolate Manufacture”)，R.Lees 和 E.B.Jackson，化工出版社，1975 年 2 月 7 日，以及“工业巧克力制造和使用”(Industrial Chocolate Manufacture and Use)，编辑，S.T.Beckett，布莱基 & 索恩公司 (Blackie&Son Ltd.)，格拉斯哥 (Glasgow)，1988 中描述了此类方法，由此每个文件通过整体引用合并于此以用于任何和所有目的。

[0001] 此类方法通常可通过用于实施这些方法的设备进行，此设备可为干燥设备或者制浆设备，两种类型均可从例如 Ets 迪穆兰 & 公司 (Ets Dumoulin&Cie)，图尔南 - 布里 (Tournan-en Brie)，法国，KOCO 食品技术公司 (KOCO Food Tech,Inc.)，菲尼克斯 (Phoenix)，MD 和 Loynds 国际有限公司 (MD and Loynds International,Ltd.)，波尔顿 Le 法尔德 (Poulton Le Fylde)，英国，商购。

[0084] 抛光在此与膜状包衣形成对比，即，包衣通过抛光法涂覆，而不是膜状包衣法。尽管两种方法都是用于制备被涂布的可食用产品，例如糖食和药物的工业方法，但它们是利用非常不同的涂布制剂的非常不同的方法。抛光和一些涂布过程在转筒或“盘”中进行。通常，对于将糖类包衣，诸如蔗糖、右旋糖，涂覆至大量夹心以制造有糖衣的产品，使用术语“抛光”。对于将不是基于糖的包衣涂覆至大量夹心，使用术语“膜状包衣”，其中包衣材料通常包括成膜组分，诸如改性纤维素，例如羟丙基甲基纤维素，包衣被连续涂覆至夹心，直至实现所需包衣厚度。常规的抛光包衣不包括成膜组分，也不包括本发明的抛光包衣。

[0085] 在硬抛光过程中，多次施用高浓度的糖浆用于在可食用产品夹心上形成糖的包衣的无色部分。其后为多次施用含着色剂的浓糖浆。硬抛光过程包括将包衣溶液或组合物的薄层重复施用至混合夹心，同时混合大部分夹心，并干燥每个包衣溶液或组合物的层，在此期间包衣中的糖在施用各个层之间结晶。相反，由于膜状包衣方法不需要糖的包衣结晶，膜状涂布是连续方法，通常包括同时施用包衣溶液，通过包衣溶液的混合和干燥。也就是说，膜状包衣喷雾器在膜状涂布过程中不关闭，但连续运行直至施用得到所需的膜状包衣。膜状包衣溶液通常包含少于约 10wt％的固体，因为更高的浓度将粘度太大而不能喷射。然而，在每种方法中，包衣材料被堆积在夹心上，以形成所需包衣。

[0086] 如果包衣将要被着色，则在涂布过程的后期阶段，将可食用的着色剂加入到包衣

溶液中。对于硬质抛光糖食，在施用许多层无色糖浆层以形成糖的包衣之后，多次施用包括着色剂的糖浆用于提供彩色包衣。彩色包衣可需要 30 次或更多次施用着色的包衣溶液以获得所需颜色。这是因为由于糖的包衣溶液的高糖固体含量，可溶解在糖溶液中的染料的量较低。由此，形成壳的过程，包括着色步骤，可需要多个小时。

[0087] 在另一个方面，本发明涉及一种使颜色稳定化的方法，该颜色由含花青素苷的天然蓝色着色剂提供至具有多个包衣层的硬质抛光包衣，该方法包括施用多个包衣层，使得该多个包衣层都不同时含有含花青素苷的天然蓝色着色剂和食品级碳酸钙。

[0088] 现将参照以下实施例阐述本发明的具体实施方式。应理解，公开这些实施例仅用于说明本发明，且在本发明的主旨内的变体是可预期的。

实施例 1

不同的环境条件下第一包衣糖浆的添加剂对硬质抛光糖食的颜色稳定性的影响，该硬质抛光糖食用含花青素苷的天然蓝色着色剂着色

[0089] 糖基包衣通过硬抛光方法涂覆至扁豆状的巧克力夹心上。用去离子水制备 74° 白利度 (Brix) 糖 (蔗糖) 浆。通过将 75 克的液态红球甘蓝提取物 (San Red RCFU, San-Ei Gen F. F. I. (USA), Inc. (三荣源), New York(纽约), NY) 与 1 克粉状紫甘薯提取物 (CH 1000, 克里斯蒂安 • 汉森公司 (Chr Hansen, Inc.), 密尔沃基 (Milwaukee), 威斯康星州 (WI)) 混合并用 2M NaOH 调节至 pH 为 8 来制备含花青素苷的天然蓝色着色剂 (“NBA-1”)。由含有以 2.5wt％添加的二氧化钛的糖浆组成的第一包衣糖浆被涂覆至夹心，并干燥成 5 层。由含有以 3.7wt％添加的着色剂的糖浆组成的第二包衣糖浆被涂覆至夹心，并干燥成 17 层。经着色的夹心用抛光胶，随后是蜡的包衣完成。

[0090] 用替代的由含有以 10wt％添加的碳酸钙的糖浆组成的第一包衣糖浆重复以上方法。用仅由糖浆组成的另一替代的第一包衣糖浆再重复以上方法。第二试验和第三试验的第二包衣糖浆和最后的包衣与第一试验的相同。

[0091] 将分别来自以上三个试验的糖食片置于水活度为 0.0、0.54 和 0.75 的受控环境中，以及置于周围环境条件下的室内环境中。在第七天，对来自每个试验的每种储存条件的 10 个糖食片进行颜色测量，计算 L*a*b* 值，并计算平均值，如表 1 中所示 :

表 1

样品名称	L*	a*	b*	在 a_w = 0.0 时与含相同添加剂的样品相比的ΔE
NBA-1, TiO_2, a_w = 0.0	39.05	2.7	-22.95	---
NBA-1, TiO_2, a_w = 0.54	38.61	2.85	-22.98	0.47
NBA-1, TiO_2，周围环境水活度（Ambient）	39.05	3.49	-22.89	0.79
NBA-1, TiO_2, a_w = 0.75	39.59	7.74	-22.82	5.07
NBA-1, $CaCO_3$, a_w = 0.0	36.89	-1.78	-20.50	---
NBA-1, $CaCO_3$, a_w = 0.54	36.71	-1.52	-20.45	0.32
NBA-1, $CaCO_3$, 周围环境水活度（Ambient）	37.44	-1.28	-20.47	0.74
NBA-1, $CaCO_3$, a_w = 0.75	37.18	-2.39	-18.79	1.84
NBA-1, 糖浆, a_w = 0.0	35.74	4.77	-21.92	---
NBA-1, 糖浆, a_w =0.54	35.68	5.20	-22.19	0.51
NBA-1, 糖浆, 周围环境水活度（Ambient）	35.84	5.47	-21.89	0.71
NBA-1, 糖浆, a_w = 0.75	36.64	8.81	-19.87	4.62

[0092] 图 1 示出了每个试验样品在每个环境条件下与水活度为 0.0 时同一样品相比的 ΔE 色差值。每个样品在较高的水活度以及周围环境下经历色移，水活度为 0.75 时出现最大的色移 (color shift)，用最大的 ΔE 值表示。水活度为 0.75 时，第一包衣层中含有二氧化钛作为添加剂以及没有添加剂的试验样品的 ΔE 值分别为 5.07 和 4.62，并且指示样品中显著的色移。第一包衣层中含有碳酸钙作为添加剂的试验样品在水活度为 0.75 时具有最小色移，如用最小 ΔE 值 1.84 测定。ΔE 值 1.84 表明，水活度为 0.75 时含碳酸钙的样品的颜色将与水活度为 0.0 时的同一样品的颜色不能区分，这通过视觉观察得到证实。

实施例 2

不同的环境条件下第一包衣糖浆的添加剂对硬质抛光糖食的颜色稳定性的影响，该硬质抛光糖食用替代的含花青素苷的天然蓝色着色剂着色

[0093] 糖基包衣通过硬抛光方法涂覆至扁豆状的巧克力夹心上。用去离子水制备 74° 白利度 (Brix) 糖浆。所用着色剂为由粉状紫甘薯和紫胡萝卜提取物组成的 (CH 5000, 克里

斯蒂安·汉森公司（Chr. Hansen, Inc.），密尔沃基（Milwaukee），威斯康星州（WI））含花青素苷的天然蓝色着色剂（“NBA-2”）。由含有以 2.5wt％添加的二氧化钛的糖浆组成的第一包衣糖浆被涂覆至夹心，并干燥成 5 层。由含有以 0.5wt％添加的着色剂的糖浆组成的第二包衣糖浆被涂覆至夹心，并干燥成 17 层。经着色的夹心用抛光胶，随后是蜡的包衣完成。

[0094] 用替代的由含有以 10wt％添加的碳酸钙的糖浆组成的第一包衣糖浆重复以上方法。用另一替代的由含有以 5wt％添加的碳酸钙和以 1.25wt％添加的二氧化钛的糖浆组成的第一包衣糖浆再重复以上方法。第二试验和第三试验的第二包衣糖浆和最后的包衣与第一试验的相同。

[0095] 将分别来自以上三个试验的糖食片置于水活度为 0.0、0.54 和 0.75 的受控环境中，以及置于周围环境条件下的室内环境中。在第七天，对来自每个试验的每种储存条件的 10 个糖食片进行颜色测量，计算 L*a*b* 值，并计算平均值，如表 2 中所示：

表 2

样品名称	L*	a*	b*	在 $a_w = 0.0$ 时与含相同添加剂的样品相比的ΔE
NBA-2, TiO_2, $a_w = 0.0$	41.69	-1.09	-20.13	---
NBA-2, TiO_2, $a_w = 0.54$	40.16	0.48	-20.67	2.26
NBA-2, TiO_2，周围环境水活度（Ambient）	40.97	0.55	-20.52	1.83
NBA-2, TiO_2, $a_w = 0.75$	42.31	2.29	-19.29	3.54
NBA-2, $CaCO_3$, $a_w = 0.0$	38.80	-2.33	-18.12	---
NBA-2, $CaCO_3$, $a_w = 0.54$	38.51	-2.09	-18.2	0.38
NBA-2, $CaCO_3$，周围环境水活度（Ambient）	37.87	-1.20	-18.4	1.49
NBA-2, $CaCO_3$, $a_w = 0.75$	39.55	-1.56	-16.09	2.30
NBA-2, $TiO_2/CaCO_3$, aw = 0.0	41.32	-0.6	-20.32	---
NBA-2, $TiO_2/CaCO_3$, aw = 0.54	40.49	-0.96	-19.9	1.00
NBA-2, $TiO_2/CaCO_3$，周围环境水活度（Ambient）	40.78	-0.23	-19.94	0.76
NBA-2, $TiO_2/CaCO_3$, aw = 0.75	44.32	-2.15	-16.65	4.99

[0096] 图 2 示出了每个试验样品在每个环境条件下与水活度为 0.0 时同一样品相比的 ΔE 色差值。每个样品在较高的水活度以及周围环境下经历色移，水活度为 0.75 时出现最大的色移，用最大的 ΔE 值表示。水活度为 0.75 时，第一包衣层中含有二氧化钛作为添加剂以及含有二氧化钛和碳酸钙一起作为添加剂的试验样品的 ΔE 值分别为 3.54 和 4.99，并且指示样品中显著的色移。第一包衣层中含有碳酸钙作为添加剂的试验样品在水活度为 0.75 时具有最小色移，如用最小 ΔE 值 2.30 测定。ΔE 值 2.30 表明，水活度为 0.75 时含碳酸钙的样品的颜色将与水活度为 0.0 时的同一样品的颜色不能区分，这通过视觉观察得到证实。

实施例 3

不同的金属盐作为第一包衣糖浆的添加剂对硬质抛光糖食的颜色稳定性的影响，该硬质抛光糖食用含花青素苷的天然蓝色着色剂着色

[0097] 用不同的金属盐作为用于制造硬质抛光糖食的第一包衣糖浆的添加剂进行实验，该硬质抛光糖食用含花青素苷的天然蓝色着色剂着色。目的是比较含有一价阳离子的碳酸盐相对于含有二价阴离子的碳酸钙的影响。而碳酸钙基本不溶于水，碳酸钠和碳酸钾溶于水。这导致它们影响糖浆的 pH，由此影响含花青素苷的着色剂在糖浆中的颜色，并且不能对包衣提供乳浊化作用。因此，将二氧化钛与替代的碳酸盐组合使用，以提供所需的不透明性。

[0098] 还测试了不溶的硫酸钙作为碳酸钙的替代物与二氧化钛的组合，以评定碳酸钙的作用与被存在的钙离子“固定”的花青素苷颜色是否有关的原因。

[0099] 糖基包衣通过硬抛光方法涂覆至扁豆状的巧克力夹心上。用去离子水制备 74° 白利度 (Brix) 糖浆。所用着色剂为由粉状紫甘薯和紫胡萝卜提取物组成的 (CH 5000, 克里斯蒂安•汉森公司 (Chr Hansen, Inc.), 密尔沃基 (Milwaukee), 威斯康星州 (WI)) 含花青素苷的天然蓝色着色剂 (“NBA-2”)。由含有以 10wt％添加的碳酸钙的糖浆组成的第一糖浆被涂覆至夹心，并干燥成 5 层。由含有以 0.5wt％添加的着色剂的糖浆组成的第二糖浆被涂覆至夹心，并干燥成 17 层。经着色的夹心用抛光胶，随后是蜡的包衣完成。

[0100] 用替代的由含有以 1wt％添加的碳酸钠和以 2.5wt％添加的二氧化钛的糖浆组成的第一包衣糖浆再重复以上方法。用另一替代的由含有以 1wt％添加的碳酸钾和以 2.5wt％添加的二氧化钛的糖浆组成的第一包衣糖浆再重复以上方法。用又一替代的由含有以 1wt％添加的碳酸钙和以 2.5wt％添加的二氧化钛的糖浆组成的第一包衣糖浆再重复以上方法。第二试验至第四试验的第二包衣糖浆和最后的包衣与第一试验的相同。

[0101] 对来自每个试验的 10 种糖食片进行颜色测量，计算 L*a*b* 值，并计算平均值，如表 3 中所示：

表 3

样品名称	L*	a*	b*	Δ与含有 $CaCO_3$ 作为添加剂的样品相比的ΔE
NBA-2, $CaCO_3$	41.69	-1.09	-20.13	---
NBA-2, Na_2CO_3/TiO_2	37.87	-1.20	-18.40	16.70
NBA-2, K_2CO_3/TiO_2	35.59	-9.78	-4.25	17.82
NBA-2, $CaSO_4/TiO_2$	31.12	-9.55	-4.18	8.96

[0102] 与含有碳酸钙作为第一包衣糖浆中添加剂的本发明的样品相比，含有替代的金属盐作为添加剂的其它样品分别提供约 9 或更大的 ΔE 色差值，指示显著的色差。也就是说，替代的金属盐不能对用于抛光涂布的含花青素苷的天然蓝色着色剂提供与碳酸钙相同的稳定化作用。此外，将碳酸钠和二氧化钛一起用作第一包衣糖浆中的添加剂导致不能接受的双色质 (two-toned) 的抛光包衣颜色。测试结果表明由碳酸钙提供的颜色稳定化作用不会归因于钙离子的色“固定作用”，也不会归因于溶液中存在二价阳离子，因为碳酸钙不溶于水。

实施例 4

不同环境条件下，在糖浆中使用自来水 (tap water) 以及在第一包衣糖浆中使用碳酸钙对硬质抛光糖食的颜色稳定性的影响，该硬质抛光糖食用含花青素苷的天然蓝色着色剂着色

[0103] 糖基包衣通过硬抛光方法涂覆至扁豆状的巧克力夹心上。用含有少量金属离子，如钙、钠和镁的未经处理的自来水 (Tap) 制备 74° 白利度 (Brix) 糖浆。所用的着色剂与实施例 1 中相同，“NBA-1”。由含有以 10wt％添加的碳酸钙的糖浆组成的第一包衣糖浆被涂覆至夹心，并干燥成 5 层。由含有以 3.7wt％添加的着色剂的糖浆组成的第二包衣糖浆被涂覆至夹心，并干燥成 17 层。经着色的夹心用抛光胶，随后是蜡的包衣完成。

[0104] 将来自上述试验的糖食片置于水活度为 0.0、0.54 和 0.75 的受控环境中，以及置于周围环境条件下的室内环境中。在第七天，对来自每种储存条件的 10 个糖食片进行颜色测量，计算 L*a*b* 值，并计算平均值，如表 4 中所示，以及对实施例 1 中含碳酸钙的试验样品获得的 L*a*b* 值，实施例 1 中含碳酸钙的试验样品使用用去离子水 (DI) 制备的糖浆：

表 4

样品名称	L*	a*	b*	在 a_w = 0.0 时与“Tap”样品相比的ΔE
NBA-1, $CaCO_3$, Tap, a_w = 0.0	36.47	-0.61	-22.11	---
NBA-1, $CaCO_3$, Tap, a_w = 0.54	36.55	-0.49	-22.23	0.19
NBA-1, $CaCO_3$，Tap，周围环境水活度（Ambient）	36.33	0.28	-22.16	0.90
NBA-1, $CaCO_3$, Tap, a_w = 0.75	36.91	0.63	-21.30	1.55
				在 a_w = 0.0 时与“DI”样品相比的ΔE
NBA-1, $CaCO_3$, DI, a_w = 0.0	36.89	-1.78	-20.50	---
NBA-1, $CaCO_3$, DI, a_w = 0.54	36.71	-1.52	-20.45	0.32
NBA-1, $CaCO_3$, DI, 周围环境水活度（Ambient）	37.44	-1.28	-20.47	0.74
NBA-1, $CaCO_3$, DI, a_w = 0.75	37.18	-2.39	-18.79	1.84

[0105] 图 3 示出了每个试验样品在每个环境条件下与水活度为 0.0 时同一样品相比的 ΔE 色差值。每个样品在较高的水活度以及周围环境条件下经历色移，水活度为 0.75 时出现最大的色移，用最大的 ΔE 值表示。然而，在糖浆中使用去离子水的样品和使用自来水的样品之间未看出明显差异。

[0106] 本发明实施方式的上述描述仅用于说明，并不应被认为限制本发明，本发明由所附权利要求限定。

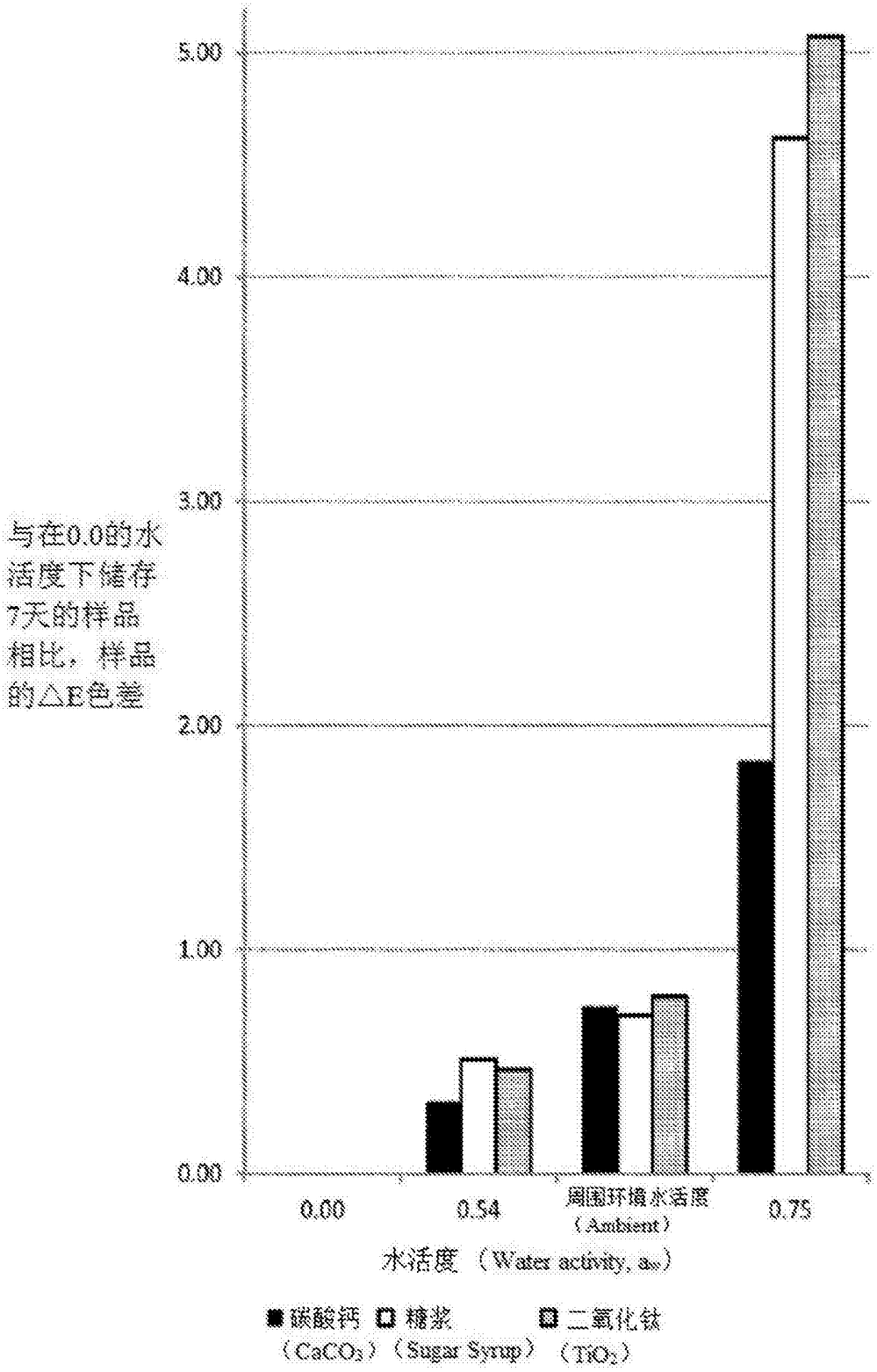
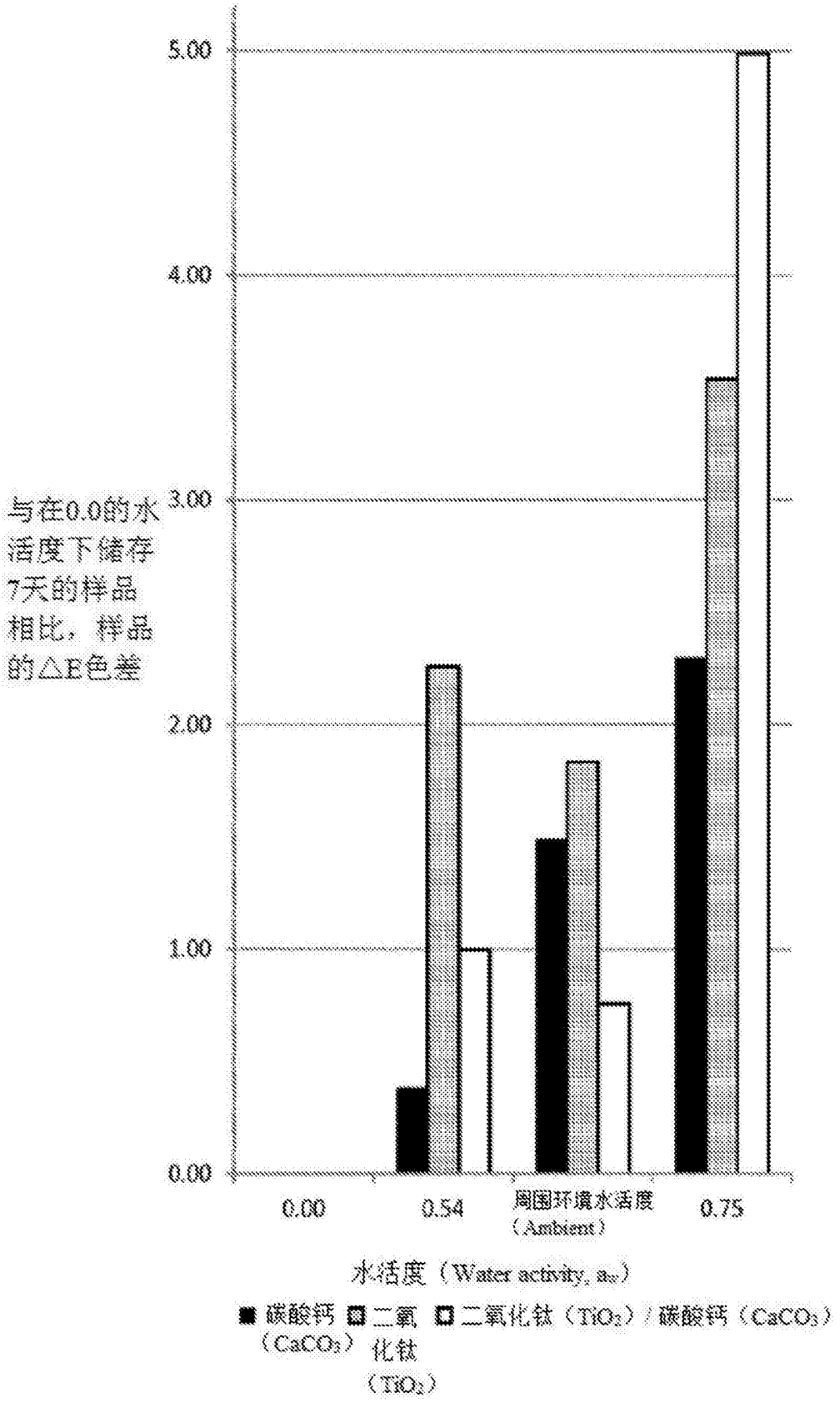

5.00
4.00
3.00
2.00
1.00
0.00
与在0.0的水活度下储存7天的样品相比，样品的△E色差
0.00
0.54
周围环境水活度（Ambient）
0.75
水活度（Water activity, a_w）
碳酸钙（$CaCO_3$）
糖浆（Sugar Syrup）
二氧化钛（TiO_2）

图 1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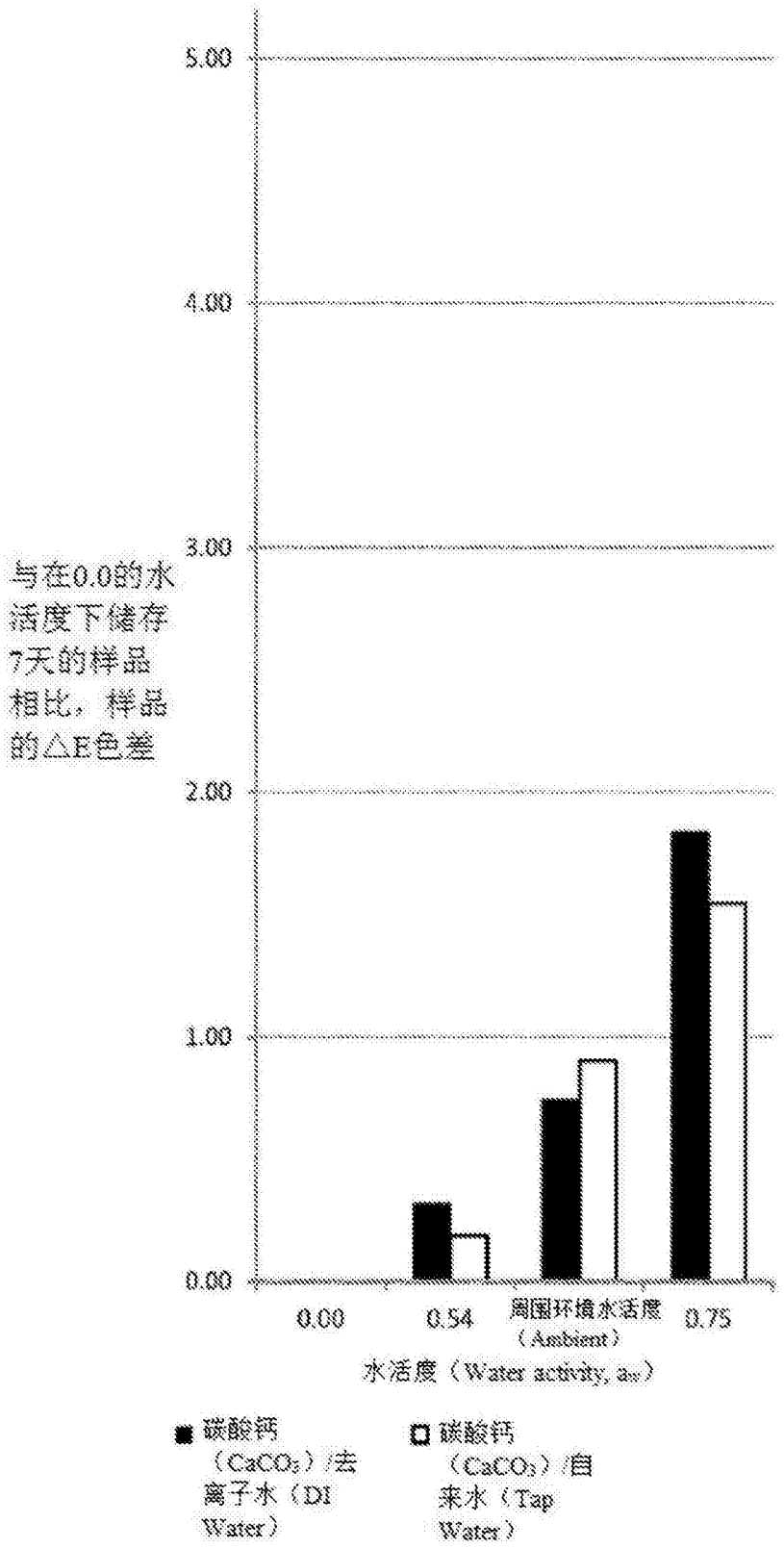
与在0.0的水活度下储存7天的样品相比，样品的△E色差
0.00
0.54
周围环境水活度（Ambient）
0.75
水活度（Water activity, a_w）
碳酸钙（$CaCO_3$）
二氧化钛（TiO_2）
二氧化钛（TiO_2）/碳酸钙（$CaCO_3$）

图 2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与在0.0的水活度下储存7天的样品相比，样品的△E色差
0.00
0.54
周围环境水活度（Ambient）
0.75
水活度（Water activity, a_w）
碳酸钙（$CaCO_3$）/去离子水（DI Water）
碳酸钙（$CaCO_3$）/自来水（Tap Water）

图 3

Abstract

The present invention is directed to a hard panned coating comprising a natural blue anthocyanin-containing colorant, a hard panned confection coated with the same, and a method of hard pan coating an edible product center with the coating such that the color provided by the natural blue anthocyanin-containing colorant to the coating is stabilized.