



- (51) **International Patent Classification:**
C09B 61/00 (2006.01) *C09B 67/20* (2006.01)
- (21) **International Application Number:**
PCT/CN2015/081260
- (22) **International Filing Date:**
11 June 2015 (11.06.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (71) **Applicant:** DSM IP ASSETS B.V. [NL/NL]; Het Overloon 1, 6411 TE Heerlen (NL).
- (72) **Inventors:** HITZFELD, Andrea; Wurmisweg 576, Kaiseraugst, CH-4303 (CH). HUANG, Xiaoping; No. 476, Li Bing Rd., Zhangjiang High-Tech Park, Pudong New Area, Shanghai 201203 (CN). HE, Qing; No. 476, Li Bing Rd., Zhangjiang High-Tech Park, Pudong New Area, Shanghai 201203 (CN). KÖNIG-GRILLO, Simone; Wurmisweg 576, 4303 Kaiseraugst (CH).
- (74) **Agent:** BEIJING EAST IP LTD.; Suite 1601, Tower E2, The Towers, Oriental Plaza, No.1 East Chang An Ave., Dongcheng District, Beijing 100738 (CN).

- (81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) **Title:** NEW GREEN COLOR FOR EDIBLE COATINGS

(57) **Abstract:** A green edible coating comprises Gardenia Blue pigment and vitamin B₂ (derivatives). This edible coating has a color shade h of at least 90 at the CIELAB color scale and preferably also a color value b* of at least 10 at the CIELAB color scale. This edible coating is preferably used for coating confectionary such as chocolate lentils. The present invention is also directed to precursors of such green edible coatings such as sugar syrup and sugar-free alternatives, both comprising Gardenia Blue pigment and Vitamin B₂ (derivatives).



WO 2016/197369 A1

NEW GREEN COLOR FOR EDIBLE COATINGS

The present invention is directed to green edible coatings which are e.g. used for confectionaries such as in particular chocolate products. The present invention is further directed to the precursors of such green edible coatings, i.e. the green sugar syrup or the green sugar-free syrup, as well as to panned confection and a process for its manufacture.

There is increasing interest in the food industry to replace synthetic materials for coloring foods with natural or nature identical colorants. Especially wanted are colors that are also animal-free and kosher/halal.

A 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 and to match the color of the product the consumer is already used to. Thus, it is important that a consistent visual quality of the product is guaranteed.

Surprisingly it has been found that a mixture of Gardenia Blue pigment and vitamin B₂ (derivatives) can be used to impart a green color to edible coatings. In a preferred embodiment of the present invention the Gardenia Blue pigment and the vitamin B₂ (derivatives) are the only colorants used in the edible coating.

In a further preferred embodiment of the present invention the edible coating does not contain any emulsifiers. Especially preferred in this respect is an edible coating according to the present invention that does neither contain Arabic Gum nor modified food starch (such as OSA starch) nor phospholipids nor glycerides nor sucrose esters nor sorbitan esters nor propylene glycol esters which are all used as emulsifiers.

Thus, the present invention is directed to a green edible coating comprising Gardenia Blue pigment and vitamin B₂ (derivatives). This edible coating can be applied to any desired edible product center.

- 5 The “Gardenia Blue pigment” according to the present invention is defined in more detail below.

Edible product center

- 10 The edible product centers may be classified as follows: soft, hard, filled, extruded and compressed edible product centers.

Examples of soft edible product centers are deposited products based on Gum Arabic, gelatin, agar agar and/or pectin; toffee mass; deposited foam and fondant.

15

Examples of hard edible product centers are hard boiled candy, all types of nuts and recrystallized candy mass.

- 20 Examples of filled edible product centers are crusted liquid filling (coffee beans, easter eggs), soft candy with powder filling and soft candy with semi liquid filling.

Examples of extruded edible product centers are expanded cereals, original liquorice and fruit liquorice.

25

Examples of compressed edible product centers are all type of mint and fruit tablets, as well as drug delivery systems.

- 30 The edible product center may also be characterized according to the material it is made of. Therefore, in some embodiments, the edible product center may comprise a natural center, e.g., a nut (e.g. almonds, peanuts, hazelnuts), a nut

paste, a fruit (e.g. a date), a dried fruit (e.g. dried apricots or raisins) or dried fruit pieces, or dried fruit paste, or spices (e.g. coriander, ginger, anisette seeds). The edible product center may also be sugar crystals.

- 5 Or, the edible product center may comprise a confection, e.g., a boiled sugar syrup, caramel, nougat, toffee, marshmallows, fudge, chocolate, or combinations of these.

10 Alternatively, the edible product center may comprise a grain-based item such as cereals (e.g. oat, wheat, corn, rice), e.g., a cookie, pretzel, biscuit, wafer, cracker, or other baked, crisped, or puffed material.

The edible product center may also be a tablet or a chewing gum. Examples of a tablet are a pharmaceutical or a (multi)vitamin tablet or a (multi)mineral
15 tablet or a mixture thereof. The chewing gum can be in the form of balls, pillows or compressed tablets.

Edible coating

The edible coating of the present invention which comprises a mixture of
20 Gardenia Blue pigment and vitamin B₂ (derivatives) has preferably a color shade h of at least 90 at the CIELAB Color scale, more preferably it has a color shade h is in the range of from 95 to 125 at the CIELAB Color scale, most preferably the color shade h of the edible coating comprising a mixture of Gardenia Blue pigment and vitamin B₂ (derivatives) is in the range of from 100
25 to 120 at the CIELAB Color scale.

In a preferred embodiment of the present invention such an edible coating of the present invention which comprises a mixture of Gardenia Blue pigment and vitamin B₂ (derivatives) has preferably also a color value b* of at least 10 at the
30 CIELAB Color scale, more preferably the color value b* is in the range of from

12 to 35 at the CIELAB Color scale, most preferably the color value b^* is in the range of from 13 to 32 at the CIELAB Color scale.

5 Since the Gardenia Blue pigment is water-soluble, it may be used as such or as aqueous solution.

Gardenia Blue Pigment

The Gardenia Blue pigment is preferably obtained by a process comprising the following steps:

- 10 a) Treating geniposide with a glycosidase to obtain a hydrolysate; and
- b) Extracting the hydrolysate obtained in step a) with a solvent and removing the solvent after the extraction to obtain a product comprising genipin; and
- 15 c) Reacting the product comprising genipin obtained in step b) with an aqueous solution of an amino acid and/or a salt thereof to produce the Gardenia Blue pigment, and preferably dissolving the product comprising genipin in a water-soluble solvent resulting in a solution and using the solution as such; and
- 20 d) Optionally, purifying the Gardenia Blue pigment produced in step c).

The Gardenia Blue pigment obtained by the process above is sky blue, brighter than the blue such as ultramarine blue produced by the known processes as e.g. disclosed in WO 06/082922, WO 03/029358 and JP8067828.

- 25 In the above process, the geniposide used as raw material may be from various sources. It may be obtained by extracting the fruit *Gardenia Jasminoides Ellis* by any known process, for example, that as disclosed in Chinese patent publication CN102732050A. In addition, geniposide powders, which contain about 20 weight-% to about 70 weight% of geniposide and are commercially
- 30 available, and the waste stream from the Gardenia Yellow production, which contains about 40 weight-% of geniposide and is also commercially available,

may be used into the process directly or after simple refining (see CN103509368A, CN103525883A *etc.*).

5 The glycosidase used in step a) is an enzyme under EC 3.2.1 according to the Recommendations of the Nomenclature Committee of the International Union of Biochemistry and Molecular Biology on the Nomenclature and Classification of Enzymes by the Reactions they Catalyse. Preferably, the glycosidase is cellulase (EC 3.2.1.4) and β -glucosidase (EC 3.2.1.21). The examples of the glycosidase include but are not limited to cellobiase commercially available
10 from Sunson Biotechnology Co. Ltd. (Guangzhou, China), Cellulase 4000 commercially available from DSM (China) Ltd. (Shanghai, China), and Rapidase®, commercially available from DSM (China) Ltd. (Shanghai, China).

15 The glycosidase may be added into the reaction of the step a) in an amount in the range of from 0.01 g to 0.8 g, preferably in an amount in the range of from 0.05 g to 0.5 g, more preferably in an amount in the range of from 0.1 g to 0.3 g, per 1 g of geniposide.

20 The treatment of the step a) may be carried out at a pH in the range of from 3.0 to 6.5, preferably at a pH in the range of from 3.6 to 6.0, and more preferably at a pH in the range of from 4.0 to 4.6. Preferably, the treatment of the step a) is carried out in a buffer solution which can provide the above pH ranges. Such buffer solution is known in the art, and the examples include but are not limited to an aqueous HCOOH/NaOAc solution or an aqueous citric
25 acid/ Na_2HPO_4 solution. The buffer solution may be added in an amount in the range of from 8 mL to 80 mL, preferably in an amount in the range of from 10 mL to 50 mL, more preferably in an amount in the range of from 20 mL to 40 mL, per 1 g of geniposide.

30 The treatment of the step a) may be carried out at a temperature in the range of from about 20°C to about 60°C, preferably at a temperature of about 50°C.

The reaction of the step a) may last about 10 hours to about 30 hours. The obtained hydrolysate contains genipin as main component and other components. The hydrolysate can be used for the extraction in step b) directly.

5

Any person skilled in the art could understand that, the solvent used for extraction in the step b) is important and may be any one suitable for this purpose, and examples include but are not limited to diethyl ether, ethyl acetate, butanol, a mixture of butanol with petroleum and/or hexane, or mixtures thereof. In the embodiment that the solvent is a mixture of butanol with petroleum and/or hexane, the volume ratio of butanol with hexane and/or hexane is in the range of from 1:5 to 5:1, preferably in the range of from 1:3 to 3:1, and more preferably in the range of from 1:2 to 2:1.

10

The amount of the solvent used in the step b) may be from 1 mL to 5 mL, preferably from 1.5 mL to 3 mL, per 1 mL of the hydrolysate. The extraction of the step b) may be carried out at a temperature in the range of from 10°C to 60°C, preferably at room temperature. According to the present invention, the extraction of the step b) may be repeated two to four times.

20

The product comprising genipin is obtained after the organic phases are collected and the solvent is removed in the step b). The solvent may also be recycled. The extraction procedures and the procedures for collecting solvents and removing/recycling solvents during the extraction are known to the person skilled in the art. Therefore, they are not discussed in more detail here.

25

As known in the art, the Gardenia Blue pigment is the reaction product of genipin with an amino acid or a salt thereof. Accordingly, as the step c) of the process, the product comprising genipin obtained in the step b) is reacted with an amino acid or a salt thereof to produce the Gardenia Blue pigment. In the present invention, the amino acid suitable for the reaction may be selected

30

from the group consisting of glutamate, phenylalanine, histidine, leucine, isoleucine, arginine and mixture thereof. The salt may be any alkali metal salt such as sodium salt. Preferably the salt is sodium glutamate. The inventors of the present invention discovered that the amino acid and the salt used in the
5 step c) are also important because they can provide sky blue color as disclosed in the present invention.

In the present invention, an aqueous solution of the amino acid or the salt thereof is used to react with the product comprising genipin to provide the
10 Gardenia Blue pigment and the aqueous solution is added in an amount to provide a molar ratio of 1: 0.5-2, preferably 1: 0.7-1.5 between genipin and the amino acid in the reaction mixture of step c).

In addition, the inventors of the present invention discovered that it would be
15 helpful for the reaction in the step c) to dissolve the product comprising genipin in a water-soluble solvent to form a homogeneous reaction system. Accordingly, the product comprising genipin obtained from the step b) is preferably dissolved in a water-soluble solvent according to the present invention. The water-soluble solvent may be any one known in the art that can
20 dissolve the product comprising genipin and examples include but are not limited to C₁₋₁₀ alkanols such as methanol and ethanol, and C₃₋₁₀ ketones such as acetone. Preferably, the water-soluble solvent is methanol, ethanol or acetone or any mixture thereof.

25 The reaction of the step c) may be carried out at about 40°C to about 75°C. The progress of the reaction can be monitored by any known method, such as HPLC and TLC.

After the reaction is complete, the Gardenia Blue pigment can be obtained as a
30 solid by removing the organic solvent and water in the reaction mixture. Accordingly, the process of the present invention optionally further comprises

the step of removing the solvent and water to provide a solid of the Gardenia Blue pigment by, for example, lyophilization or spray drying.

5 Optionally, the obtained Gardenia Blue pigment can be purified further by any procedures known in the art such as ultrafiltration to obtain an even purer Gardenia Blue pigment.

10 The process of the present invention produces the Gardenia Blue pigment which is sky blue, brighter than the blue color such as ultramarine blue produced by the known processes. Further, by an additional extraction step, the obtained Gardenia Blue pigments can surprisingly be easily separated and purified from the reaction mixture without complicated operations.

Vitamin B₂ and its derivatives

15 Vitamin B₂, also called riboflavin, has a poor solubility in water.

Thus, preferably water-soluble derivatives of vitamin B₂/riboflavin are used such as e.g. and most preferred riboflavin-5-phosphate.

20 Amount of Vitamin B₂ and its derivatives in the edible coating

Preferably the amount of Vitamin B₂ or its derivatives (preferably the amount of water-soluble Vitamin B₂ derivatives, more preferably the amount of riboflavin-5-phosphate) in the edible coating is in the range of from 20 ppm to 250 ppm, more preferably it is in the range of from 50 ppm to 150 ppm, most
25 preferably it is in the range of from 70 ppm to 140 ppm, based on the total weight of the edible coating.

The edible coating according to the present invention can be one being based
30 on sugar but also one being based on sugar-free alternatives.

Sugar-based edible coatings

Preferably the sugar in the edible coating is selected from the group consisting of monosaccharides and disaccharides and mixtures thereof.

- 5 Preferred examples of mono- and disaccharides are saccharose, glucose, fructose, maltose and mixtures thereof.

The sugar syrup has preferably a Brix value in the range of from 65 to 75, more preferably it has a Brix value in the range of from 70 to 75.

10

When the edible coating is a hard panned coating, the 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
15 modifiers, 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.

Sugar-free alternatives

- 20 Sugar-free edible coatings are also part of the present invention. Here polyols such as maltitol, xylitol, mannitol, sorbitol, isomalt, palatinose and mixtures thereof are used instead of sugar.

Product

- 25 The present invention is directed to the edible coating as described above and claimed in the claims.

Furthermore, the present invention is also directed to a sugar syrup comprising a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives
30 (preferably a mixture of Gardenia Blue pigment and water-soluble vitamin B₂ derivatives, more preferably a mixture of Gardenia Blue pigment and

riboflavin-5-phosphate), wherein the sugar is selected from the group consisting of monosaccharides and disaccharides and mixtures thereof. Preferably the sugar is selected from the group consisting of saccharose, glucose, fructose, maltose and mixtures thereof.

5

The same preferences as given above for the edible coating such as e.g. kind of vitamin B₂ derivative and its amount, etc. also apply for the sugar syrup.

The present invention is also directed to a sugar-free syrup comprising a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives (preferably a mixture of Gardenia Blue pigment and water-soluble vitamin B₂ derivatives, more preferably a mixture of Gardenia Blue pigment and riboflavin-5-phosphate) and a polyol, wherein the polyol is selected from the group consisting of maltitol, xylitol, mannitol, sorbitol, isomalt, palatinose and mixtures thereof.

15

The same preferences as given above for the edible coating such as e.g. kind of vitamin B₂ derivative and its amount, etc. also apply for the sugar-free syrup.

20 The invention is also directed to a panned confection comprising:

- a) an edible product center as described above, and
- b) and edible coating with the preferences as described above.

An especially preferred embodiment of the present invention is sugar coated chocolate confectionary whereby a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives (preferably a mixture of Gardenia Blue pigment and water-soluble vitamin B₂ derivatives, more preferably a mixture of Gardenia Blue pigment and riboflavin-5-phosphate) results in sugar coated candies/chocolate lentils with a color shade h of at least 90 at the CIELAB Color scale (preferred with a color shade h in the range of from 95 to 125 at the CIELAB Color scale; more preferred with a color shade h in the range of from 100 to 125 at the CIELAB Color scale) and preferably also a color value b* of at

25

30

least 10 (preferred in the range of from 12 to 35; more preferred in the range of from 13 to 32) at the CIELAB Color scale.

Such a sugar coated chocolate confectionary with a color shade h of at least 90 at the CIELAB Color scale and preferably also a color value b* of at least 10 at the CIELAB Color scale comprising a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives (preferably a mixture of Gardenia Blue pigment and water-soluble vitamin B₂ derivatives, more preferably a mixture of Gardenia Blue pigment and riboflavin-5-phosphate) in the edible coating can be prepared according to a process comprising the following steps:

a) applying a minimum of 70 coating layers of sugar syrup on the confectionary;

b) optionally applying 10 layers of titanium dioxide;

c) applying 15 to 50 colored coating layers whereby the colored coating layers comprise a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives (preferably a mixture of Gardenia Blue pigment and water-soluble vitamin B₂ derivatives, more preferably a mixture of Gardenia Blue pigment and riboflavin-5-phosphate).

Processes of the present invention

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 saccharose sugar syrup.

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.

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

coating layer comprising a sugar and a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives (preferably a mixture of Gardenia Blue pigment and water-soluble vitamin B₂ derivatives, more preferably a mixture of Gardenia Blue pigment and riboflavin-5-phosphate) to the edible product center.

The colored coating layers containing a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives (preferably a mixture of Gardenia Blue pigment and water-soluble vitamin B₂ derivatives, more preferably a mixture of Gardenia Blue pigment and riboflavin-5-phosphate) may be applied in 15 to 50 colored coating layers. Preferably a minimum of 70 coating layers of sugar syrups and 10 layers of titanium dioxide have been applied before the colored coating layers containing a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives (preferably a mixture of Gardenia Blue pigment and water-soluble vitamin B₂ derivatives, more preferably a mixture of Gardenia Blue pigment and riboflavin-5-phosphate) are applied. That means that preferably a total amount of 95 to 130 coating layers is applied.

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 by a series of syrup application and drying cycles carried out, for example, in a rotating pan.

Panning and some coating processes are performed in a rotating drum or "pan". Such processes may typically be driven by the equipment utilized to perform them, which are e.g. commercially available from Friedhelm Stechel GmbH (Germany), from Wolf Spezialmaschinen (Germany) and from Driam Anlagenbau GmbH (Germany), Dumoulin (France).

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 a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives (preferably a mixture of Gardenia Blue pigment and water-soluble vitamin B₂ derivatives, more preferably a mixture of Gardenia Blue pigment and riboflavin-5-phosphate). 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. However, in each process, coating material is built up on the center to form the desired coating.

As the coating is to be colored green a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives (preferably a mixture of Gardenia Blue pigment and water-soluble vitamin B₂ derivatives, more preferably a mixture of Gardenia Blue pigment and riboflavin-5-phosphate) 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 mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives (preferably a mixture of Gardenia Blue pigment and water-soluble vitamin B₂ derivatives, more preferably a mixture of Gardenia Blue pigment and riboflavin-5-phosphate) are applied to provide the color coat. The color coat requires 15 to 50 applications of the colored coating solution to achieve the desired color.

The coating layers of the hard panned confection may be applied to any desired edible product center as described above.

In another aspect, the present invention is directed to a method of soft pan coating an edible product center as described above.

Soft pan coating

5 Soft pan coating or also called “soft panning” involves applying a syrup to the edible product centers in the same way as for hard panning; however, the soft panning syrup is intended not to crystalize. Therefore, either glucose or a mixture of sucrose and glucose is used as soft panning syrup. The centers are wetted with the syrup just sufficiently to coat them. Instead of evaporating the
10 water as in hard panning, powdered sugar or caster sugar is added during the tumble which is dissolving in the water of the applied syrup. The amount of sugar that is added needs to be just sufficient to coat the centers but has not to be in excess. Soft panning is carried out without heating and without the use of drying air. Soft panning is a much more rapid process than hard panning and
15 can be applied to a soft center that will be unsuitable for hard panning. Soft panning puts on thicker layers than hard panning and consequently the shape of the centers will be lost. A product that has been soft panned can be finished by dusting with milled sugar followed by a number of hard panned coats. Typical soft panned products are jelly beans and dolly mixture components. Typically 3
20 to 10 layers are added in soft panning.

Use according to the present invention

The present invention is also directed to the use of a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives (preferably a mixture of Gardenia
25 Blue pigment and water-soluble vitamin B₂ derivatives, more preferably a mixture of Gardenia Blue pigment and riboflavin-5-phosphate) for coloring sugar syrups, sugar-free syrups and edible coatings green, especially with a color shade h and preferably also a color value b* at the CIELAB color scale as given above.

30

The present invention is especially directed to the use of a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives (preferably a mixture of Gardenia Blue pigment and water-soluble vitamin B₂ derivatives, more preferably a mixture of Gardenia Blue pigment and riboflavin-5-phosphate) to impart a color shade h of at least 90 at the CIELAB Color scale (preferred values of h as given above) and preferably also a color value b* of at least 10 at the CIELAB color scale (preferred values of b* as given above) to sugar coated confectionary, i.e. confectionary with an edible coating according to the present invention wherein the edible coating comprises sugar and the confectionary is preferably chocolate lentils.

Color measurement

Color (lightness, Chroma, and hue) of the hard sugar coated confectionary was determined with a HunterLab Ultra Scan Pro spectrophotometer (Hunter Associates Laboratory, Reston, VA, USA) and expressed on basis of the CIELAB color scale. The mode used was RSIN which stands for Reflectance - Specular Included. The small area view (SAV) with a diameter of 4.826 mm (0.190 inch) was chosen. Color measurements are carried out after CIE guidelines (Commission International d'Eclairage). Values can be expressed as planar coordinates as L*, a*, b* with L* being the measuring values for lightness, with a* being the value on the red-green axes and b* being the value on the yellow-blue axes.

The Chroma (C*) sometimes called saturation describes the vividness or dullness of a color which can be calculated as followed:

$$C^* = \sqrt{a^{*2} + b^{*2}}$$

The angle called hue (h) describes how we perceive an object's color and can be calculated as followed:

$$h = \tan^{-1}(b/a)$$

Instruments settings:

- Color scale is the CIE L*a*b*/L*C*h
- Light source definition: D65 daylight equivalent
- 5 • Geometry: Diffuse/8°
- Wavelength: scan 350-1050 nm
- Sample measurement area diameter: 4.826 mm
- Calibration mode: Reflection/ Specular-included

10 The invention is now further illustrated in the following non-limiting examples.

Example 1: Preparation of the Gardenia Blue pigment

10 g of waster water of gardenia yellow (40 weight-% of geniposide) purchased from Qianjiang Green Sea Treasury Biotechnology Co., Ltd. (Hubei, China) was
15 added into 70 ml of an aqueous citric acid/Na₂HPO₄ buffer solution (pH 4.6). 2 g of cellobiase purchased from Sunson Biotechnology Co. Ltd. (Guangzhou, China) was further added for reaction for 30 hours under 50°C. After having cooled down the reaction mixture to room temperature, the reaction mixture was extracted with 120 ml of ethyl acetate twice. The ethyl acetate phase was
20 concentrated under vacuum to obtain rude genipin.

The obtained rude genipin was dissolved in 12 ml of absolute ethyl alcohol to obtain 11.95 g of solution (12.38 wt% of genipin by HPLC). 1.21 g of sodium glutamate in 10 ml of deionized water was added into the solution for reaction for 33 hours under 65°C.

25 The reaction liquid was lyophilized to obtain 2.9 g of gardenia blue pigment as solid powder, with a maximum absorption wavelength of 594 nm and a color value of 143.9.

Example 2: Coating of chocolate lentil cores with a mixture of Gardenia Blue
30 pigment and riboflavin-5-phosphate

A green stock solution is prepared by mixing 2 g of the Gardenia Blue pigment as obtained in example 1, and 18 g of demineralized water and 3 g of riboflavin-5-phosphate and 27 g of water, thus, dissolving the Gardenia Blue Pigment and riboflavin-5-phosphate in water.

- 5 The sugar syrup is produced by adding 600 g of sugar, 400 g of water (demineralized) and 10 g of glucose syrup together and heating the mixture up to 105°C which results in a sugar syrup of 72° Brix.

Ingredients of the sugar syrup	Amount (g)
Raw cane sugar	600
Water (demineralized)	400
Glucose Syrup	10

- 10 17 g of this Gardenia Blue pigment stock solution and 3 g of the riboflavin stock solution is mixed with 480 g of the sugar solution (65-75 Brix, preferred 70-75 Brix) at a temperature of 25°C under stirring resulting in a colored syrup.

- 15 Chocolate lentils are pre-coated with a pure sugar solution thus providing chocolate lentils with a white center. After this pre-coating a white pigment like titanium dioxide may be added to the sugar syrup and the chocolate lentils may be coated with 10-20 layers of this white sugar syrup before they are coated with the colored layers.

- 20 A small amount of colored sugar syrup is added to the chocolate lentils and evenly distributed in a panning drum at a moderate speed. Afterwards the thus colored lentils are dried with cold air (15 -25°C, relative humidity in the range 30-50%) at moderate speed resulting in one layer. These steps are repeated (usually 15-50 times) until the desired color intensity is achieved.

- 25 The hard panned candy has a smooth surface aspect which is enhanced by final glazing layers. The color values of these colored chocolate lentils were then measured and are summarized in the table below.

Example 3: Coating of chocolate lentil cores with a mixture of Gardenia Blue pigment and riboflavin-5-phosphate

A green stock solution is prepared by mixing 2 g of Gardenia Blue pigment prepared according to example 1, and 18 g of demineralized water and 3 g of riboflavin-5-phosphate and 27 g of water and, thus, dissolving the Gardenia Blue Pigment and riboflavin-5-phosphate in water.

The sugar syrup is produced by adding 600 g of sugar, 400 g of water (demineralized) and 10 g of glucose syrup together and heating the mixture up to 105 °C which results in a sugar syrup of 72 ° Brix.

Ingredients of the sugar syrup	Amount (g)
Raw cane sugar	600
Water (demineralized)	400
Glucose Syrup	10

17 g of this gardenia blue stock solution and 3 g of the riboflavin stock solution is mixed with 480 g of the sugar solution (65-75 Brix, preferred 70-75 Brix) at a temperature of 25 °C under stirring resulting in a colored syrup.

Chocolate lentils are pre-coated with a pure sugar solution thus providing chocolate lentils with a white center. After this pre-coating a white pigment like titanium dioxide may be added to the sugar syrup and the chocolate lentils may be coated with 10-20 layers of this white sugar syrup before they are coated with the colored layers.

A small amount of colored sugar syrup is added to the chocolate lentils and evenly distributed in a panning drum at a moderate speed. Afterwards the thus colored lentils are dried with cold air (15 -25 °C, relative humidity in the range 30-50%) at moderate speed resulting in one layer. These steps are repeated (usually 15-50 times) until the desired color intensity is achieved.

The hard panned candy has a smooth surface aspect which is enhanced by final glazing layers. The color values of these colored chocolate lentils were then measured and are summarized in the table below.

	Example 2	Example 3
L*	52.44	53.69
a*	-15.94	-14.94
b*	29.06	26.28
C*	33.14	30.23
h	118.75	119.61

5

Claims

1. An edible coating comprising a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives.
5
2. The edible coating according to claim 1, wherein the edible coating has a color shade h of at least 90 at the CIELAB color scale, preferably it has a color shade h in the range of from 95 to 125 at the CIELAB color scale, more preferably it has a color shade h in the range of from 100-120 at the
10 CIELAB color scale.
3. The edible coating according to claim 1 and/or 2, wherein the edible coating has a color value b* of at least 10 at the CIELAB color scale, preferably a color value b* in the range of from 12 to 35 at the CIELAB
15 color scale, more preferably a color value b* in the range of from 13 to 32 at the CIELAB color scale.
4. The edible coating according to any one or more of the preceding claims, wherein the vitamin B₂ derivative is a water-soluble vitamin B₂ derivative, preferably wherein the vitamin B₂ derivative is riboflavin-5-phosphate.
20
5. The edible coating according to any one or more of the preceding claims wherein the Gardenia Blue pigment has been obtained by a process comprising the following steps:
25
 - a) Treating geniposide with a glycosidase to obtain a hydrolysate; and
 - b) Extracting the hydrolysate obtained in step a) with a solvent and removing the solvent after the extraction to obtain a product comprising genipin; and
 - 30 c) Reacting the product comprising genipin obtained in step b) with an aqueous solution of an amino acid and/or a salt thereof to produce the Gardenia Blue pigment, and preferably dissolving the product comprising

genipin in a water-soluble solvent resulting in a solution and using the solution as such; and

d) Optionally, purifying the Gardenia Blue pigment produced in step c).

5 6. A sugar syrup comprising a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives.

7. The sugar syrup according to claim 6, wherein the sugar is selected from the group consisting of saccharose, glucose, fructose, maltose and mixtures thereof.

10

8. The sugar syrup according to claim 6 or 7, wherein the Gardenia Blue pigment has been obtained by a process comprising the following steps:

15 a) Treating geniposide with a glycosidase to obtain a hydrolysate; and
b) Extracting the hydrolysate obtained in step a) with a solvent and removing the solvent after the extraction to obtain a product comprising genipin; and

c) Reacting the product comprising genipin obtained in step b) with an aqueous solution of an amino acid and/or a salt thereof to produce the Gardenia Blue pigment, and preferably dissolving the product comprising genipin in a water-soluble solvent resulting in a solution and using the solution as such; and

20

d) Optionally, purifying the Gardenia Blue pigment produced in step c).

25 9. The sugar syrup according to any one or more of claims 6 to 8, wherein the vitamin B₂ derivative is a water-soluble vitamin B₂ derivative, preferably wherein the vitamin B₂ derivative is riboflavin-5-phosphate.

30 10. A sugar-free syrup comprising a mixture of Gardenia Blue pigment and vitamin B₂ or its derivatives and a polyol.

11. The sugar-free syrup according to claim 10, wherein the polyol is selected from the group consisting of maltitol, xylitol, mannitol, sorbitol, isomalt, palatinose and mixtures thereof.
- 5 12. The sugar-free syrup according to claim 10 or 11, wherein the Gardenia Blue pigment has been obtained by a process comprising the following steps:
- 10 a) Treating geniposide with a glycosidase to obtain a hydrolysate; and
b) Extracting the hydrolysate obtained in step a) with a solvent and removing the solvent after the extraction to obtain a product comprising genipin; and
c) Reacting the product comprising genipin obtained in step b) with an aqueous solution of an amino acid and/or a salt thereof to produce the Gardenia Blue pigment, and preferably dissolving the product comprising genipin in a water-soluble solvent resulting in a solution and using the solution as such; and
15 d) Optionally, purifying the Gardenia Blue pigment produced in step c).
13. The sugar-free syrup according to any one or more of claims 10 to 12, wherein the vitamin B₂ derivative is a water-soluble vitamin B₂ derivative, preferably wherein the vitamin B₂ derivative is riboflavin-5-phosphate.
20
14. A panned confection comprising:
a) an edible product center, and
25 b) an edible coating according to any one or more of claims 1 to 5.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2015/081260

A. CLASSIFICATION OF SUBJECT MATTER

C09B 61/00(2006.01)i; C09B 67/20(2006.01)i

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)

C09B

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)

CNTXT;CNABS;EPODOC;DWPI;CNKI;ISI WEB OF KNOWLEDGE;DSM, HITZFELD, Andrea, HUANG, Xiaoping, HE, Qing, Gardenia, Gardenia Blue, pigment, vitamin B2, derivatives, VB2, riboflavin, riboflavin 5d phosphate, color shade, natural blue pigment, edible, glucosidase, amino acid, coating, syrup, syrup d free, CIELAB, process, solvent, hydrolase, purif+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101838478 A (HENAN ZHONGDA BIOLOGY ENG CO LTD) 22 September 2010 (2010-09-22) description, paragraphs 34, 43	1-4, 6-7, 9-11, 13-14
Y	CN 101838478 A (HENAN ZHONGDA BIOLOGY ENG CO LTD) 22 September 2010 (2010-09-22) description, paragraphs 34, 43	5, 8, 12
X	CN 102613243 A (SONG X.) 01 August 2012 (2012-08-01) claim 9	1-4, 6-7, 9-11, 13-14
Y	CN 102613243 A (SONG X.) 01 August 2012 (2012-08-01) claim 9	5, 8, 12
X	CN 104017436 A (UNIV NANCHANG) 03 September 2014 (2014-09-03) claim 2	1-4, 6-7, 9-11, 13-14



Further documents are listed in the continuation of Box C.



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

14 August 2015

Date of mailing of the international search report

25 August 2015

Name and mailing address of the ISA/CN

STATE INTELLECTUAL PROPERTY OFFICE OF THE
P.R.CHINA
6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing
100088, China

Facsimile No. (86-10)62019451

Authorized officer

ZHOU, Junqing

Telephone No. (86-10)82245629

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2015/081260**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 104017436 A (UNIV NANCHANG) 03 September 2014 (2014-09-03) claim 2	5, 8, 12
Y	CN 103614431 A (UNIV NANJING TECHNOLOGY) 05 March 2014 (2014-03-05) description, paragraphs 10-24	5, 8, 12
A	JP 2008143992 A (TOYO INK MFG CO) 26 June 2008 (2008-06-26) the whole document	1-14
A	KR 20110060462 A (AMOREPACIFIC CORP) 08 June 2011 (2011-06-08) the whole document	1-14

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2015/081260

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN	101838478	A	22 September 2010	None	
CN	102613243	A	01 August 2012	None	
CN	104017436	A	03 September 2014	None	
CN	103614431	A	03 September 2014	None	
JP	2008143992	A	26 June 2008	None	
KR	20110060462	A	08 June 2011	None	