(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 December 2016 (15.12.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/197372 A1

(51) International Patent Classification:
A23L 1/275 (2006.01) *A23G 3/00* (2006.01)
A23L 1/27 (2006.01)

(21) International Application Number:
PCT/CN2015/081265

(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, 4303 Kaiseraugst (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))*

WO 2016/197372 A1

(54) Title: NEW GREEN COLOR FOR EDIBLE COATINGS

(57) Abstract: Provided is a green edible coating comprising Gardenia Blue pigment and beta-carotene. The edible coating has a color shade h of at least 95 at the CIELAB color scale and preferably also has a color value a* of at most -5 at the CIELAB color scale. The edible coating is preferably used for coating confectionary such as chocolate lentils. Also provided are precursors of such green edible coatings such as sugar syrup and sugar-free alternatives, both comprising Gardenia Blue pigment and beta-carotene.

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 beta-carotene 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 β-carotene are the only colorants used in the edible coating.

Edible coatings usually have a pH in the range of from 5-8 whereas beverages e.g. have a pH of around 3.

Thus, the present invention is directed to a green edible coating comprising a mixture of Gardenia Blue pigment and beta-carotene. This edible coating can be applied to any desired edible product center.

The "Gardenia Blue pigment" according to the present invention is defined in more detail below.

The β-carotene may be added in a water-soluble or water-dispersible form. Such a form or also called "formulation" contains the β-carotene embedded or encapsulated in a matrix of a protective colloid. Such a formulation will be explained in more detail below.

Edible product center

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.

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

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.

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

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.

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

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 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 Gardenia Blue pigment and beta-carotene has preferably a color shade h of at least 95 at the CIELAB Color scale, more preferably it has a color shade h is in the range of from 100 to 150 at the CIELAB Color scale, most preferably the color shade h of the edible coating comprising a mixture of Gardenia Blue pigment and beta-carotene is in the range of from 100 to 135 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 beta-carotene has preferably also a color value a* of at most -5 at the CIELAB Color scale, more preferably the color value a* is in the range of from -5 to -20 at the CIELAB Color scale, most preferably the color value a* is in the range of from -6 to -15 at the CIELAB Color scale.

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

Gardenia Blue Pigment

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

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
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.

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 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.*).

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 ß-glucosidase (EC 3.2.1.21). The examples of the glycosidase include but are not limited to cellobiase commercially available 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).

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.

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 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.

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.

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.

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.

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.

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 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 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 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 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 dissolve the product comprising genipin and examples include but are not limited to C_{1-10} alkanols such as methanol and ethanol, and C_{3-10} ketones such as acetone. Preferably, the water-soluble solvent is methanol, ethanol or acetone or any mixture thereof.

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 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.

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.

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.

β-Carotene

β-carotene may be synthetically manufactured or isolated from natural sources.

Amount of β-carotene in the edible coating

Preferably the amount of β-carotene in the edible coating is in the range of from 2 ppm to 100 ppm, more preferably it is in the range of from 10 ppm to 80 ppm, most preferably it is in the range of from 15 ppm to 45 ppm, based on the total weight of the edible coating.

β-carotene form

In the formulation the β-carotene is embedded in a matrix of a protective hydrocolloid. The amount of β-carotene in the formulation is usually in the range of from 1 to 15 weight-%, preferably in the range of from 2 to 10 weight-%, based on the total weight of the formulation.

The protective hydrocolloid may preferably be selected from the group consisting of modified food starch (esp. OSA starch) and proteins (of animal or plant origin) such as gelatin. Additionally water- and/or fat-soluble antioxidants may be present, preferably in an amount of from 0.5 to 5 weight-% in total, based on the total amount of the formulation.

A preferred example of such water-soluble antioxidants is sodium ascorbate.

A preferred example of such fat-soluble antioxidants is dl-alpha-tocopherol.

In an embodiment of the present invention a clear liquid formulation of β-carotene is used which comprises:

a) 0.1 to 10 weight-% (preferably 0.5 to 5 weight-%, more preferably 0.5 to 3.0 weight-%, most preferably 1.0 to 3.0 weight-%) of β-carotene, and

b) 20 to 60 weight-% (preferably 30 to 50 weight-%) of at least one modified food starch as defined below, and

c) 0.5 to 60 weight-% (preferably 0.5 to 30 weight-%, more preferably 0.5 to 20 weight-%, even more preferably 0.5 to 10 weight-%, most preferably 1.0 to 10 weight-%) of at least one saccharide, and

d) 35 to 75 weight-% (preferably 45 to 65 weight-%) of water,

all amounts based on the total weight of the liquid formulation,

whereby all amounts add up to 100 weight-%.

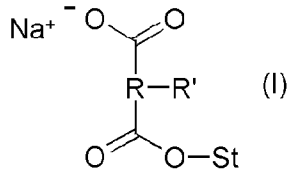
Hereby the β-carotene is embedded in a matrix of the modified food starch/es and the saccharide/s.

"Modified food starch"

A modified food starch is a food starch that has been chemically modified by known methods to have a chemical structure which provides it with a hydrophilic and a lipophilic portion. Preferably the modified food starch has a long hydrocarbon chain as part of its structure (preferably C5-C18).

At least one modified food starch is preferably used as protective hydrocolloid, but it is possible to use a mixture of two or more different modified food starches in one formulation.

Starches are hydrophilic and therefore do not have emulsifying capacities. However, modified food starches are made from starches substituted by known chemical methods with hydrophobic moieties. For example starch may be treated with cyclic dicarboxylic acid anhydrides such as succinic anhydrides, substituted with a hydrocarbon chain (see O. B. Wurzburg (editor), "Modified Starches: Properties and Uses, CRC Press, Inc. Boca Raton, Florida, 1986, and subsequent editions). A particularly preferred modified food starch of this invention has the following formula (I)



(I)

wherein St is a starch, R is an alkylene radical and R´ is a hydrophobic group. Preferably R is a lower alkylene radical such as dimethylene or trimethylene. R´ may be an alkyl or alkenyl group, preferably having 5 to 18 carbon atoms. A preferred compound of formula (I) is an "OSA-starch" (starch sodium octenyl succinate). The degree/extent of substitution, i.e. the number of esterified hydroxyl groups to the number of free non-esterified hydroxyl groups usually

varies in a range of from 0.1% to 10%, preferably in a range of from 0.5% to 4%, more preferably in a range of from 3% to 4%.

The term "OSA-starch" denotes any starch (from any natural source such as corn, waxy maize, waxy corn, wheat, tapioca and potato or synthesized) that was treated with octenyl succinic anhydride (OSA). The degree/extent of substitution, i.e. the number of hydroxyl groups esterified with OSA to the number of free non-esterified hydroxyl groups usually varies in a range of from 0.1% to 10%, preferably in a range of from 0.5% to 4%, more preferably in a range of from 3% to 4%. OSA-starches are also known under the expression "modified food starch".

The term "OSA-starches" encompasses also such starches that are commercially available e.g. from National Starch/Ingredion under the tradenames HiCap 100, Capsul, Capsul HS, Purity Gum 2000, Clear Gum Co03, UNI-PURE, HYLON VII; from National Starch/Ingredion and Roquette Frères, respectively; from CereStar under the tradename C*EmCap or from Tate & Lyle.

Saccharide

The term „saccharide" (compound c) of the clear liquid formulation of β-carotene encompasses mono-, di-, oligo- and polysaccharides, as well as any mixtures thereof.

Examples of monosaccharides are fructose, glucose (= dextrose), mannose, galactose, sorbose, as well as any mixtures thereof.

Preferred monosaccharides are glucose and fructose, as well as any mixture thereof.

The term "glucose" in the context of the present invention does not only mean the pure substance, but also a glucose syrup with a DE 90. This also applies for the other monosaccharides.

The term "dextrose equivalent" (DE) denotes the degree of hydrolysis and is a measure of the amount of reducing sugar calculated as D-glucose based on dry weight; the scale is based on native starch having a DE close to 0 and glucose having a DE of 100.

Examples of disaccharides are saccharose, isomaltose, lactose, maltose and nigerose, as well as any mixture thereof.

An example of an oligosaccharide is maltodextrin.

An example of a polysaccharide is dextrin.

An example of a mixture of mono- and disaccharides is invert sugar (glucose + fructose + saccharose).

Mixtures of mono- and polysaccharides are e.g. commercially available under the tradenames Glucidex IT 47 (from Roquette Frères), Dextrose Monohydrate ST (from Roquette Frères), Sirodex 331 (from Tate & Lyle) and Glucamyl F 452 (from Tate & Lyle).

An example of such a clear liquid formulation of β-carotene is "β-carotene 2.5% emulsion CC" as commercially available by DSM Nutritional Products AG, Kaiseraugst, Switzerland and described in detail in WO 2013/144221.

The edible coating according to the present invention can be one being based 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.

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.

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 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

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

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 beta-carotene, 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.

The same preferences as given above for the edible coating such as e.g. amount of beta-carotene, 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 beta-carotene and a polyol, wherein the polyol is selected from the group consisting of maltitol, xylitol, mannitol, sorbitol, isomalt, palatinose and mixtures thereof.

The same preferences as given above for the edible coating such as e.g. amount of β-carotene, etc. also apply for the sugar-free syrup.

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 beta-carotene results in sugar coated candies/chocolate lentils with a color shade h of at least 95 at the CIELAB Color scale (preferred with a color shade h in the range of from 100 to 150 at the CIELAB Color scale; more preferred with a color shade h in the range of from 100 to 135 at the CIELAB Color scale) and preferably also a color value a* of at most -5 (preferred in the range of from -5 to -20; more preferred in the range of from -6 to -15) at the CIELAB Color scale.

Such a sugar coated chocolate confectionary with a color shade h of at least 95 at the CIELAB Color scale and preferably also a color value a* of at most -5 at the CIELAB Color scale comprising a mixture of Gardenia Blue pigment and

beta-carotene 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 beta-carotene.

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 beta-carotene to the edible product center.

The colored coating layers containing a mixture of Gardenia Blue pigment and beta-carotene 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 beta-carotene 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 beta-carotene. 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 beta-carotene 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 beta-carotene 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

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 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 then hard panning and 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 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 beta-carotene for coloring sugar syrups, sugar-free syrups and

edible coatings green, especially with a color shade h and preferably also a color value a* at the CIELAB color scale as given above.

The present invention is especially directed to the use of a mixture of Gardenia Blue pigment and beta-carotene to impart a color shade h of at least 95 at the CIELAB Color scale (preferred values of h as given above) and preferably also a color value a* of at most-5 at the CIELAB color scale (preferred values of a* 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 spectrocolorimeter (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:

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

Instruments settings:

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

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 added into 70 ml of an aqueous citric acid/Na_2HPO_4 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 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.

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 pigment and beta-carotene

A green stock solution is prepared by mixing 2 g of the Gardenia Blue pigment as obtained in example 1, and 20 g of demineralized water and 10 g of beta-carotene 2.5% emulsion CC (as commercially available from DSM Nutritional Products AG, Kaiseraugst, Switzerland) and 20 g of water, thus, dissolving the Gardenia Blue Pigment and β-carotene 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

4 g of this Gardenia Blue pigment stock solution and 10 g of the beta-carotene stock solution are mixed with 500 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.

	Average of 10 measurements
L*	70.76
a*	-6.31
b*	30.87
C*	31.51
h	101.55

Claims

1. An edible coating comprising a mixture of Gardenia Blue pigment and beta-carotene.

2. The edible coating according to claim 1, wherein the beta-carotene is in a water-dispersible or water-soluble form.

3. The edible coating according to claim 1 and/or 2, wherein the edible coating has a color shade h of at least 95 at the CIELAB color scale, preferably it has a color shade h in the range of from 100 to 150 at the CIELAB color scale, more preferably it has a color shade h in the range of from 100 to 135 at the CIELAB color scale.

4. The edible coating according to any one or more of the preceding claims, wherein the edible coating has a color value a* of at most -5 at the CIELAB color scale, preferably a color value a* in the range of from -5 to -20 at the CIELAB color scale, more preferably a color value a* in the range of from -6 to -15 at the CIELAB color scale.

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:

   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

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

6. A sugar syrup comprising a mixture of Gardenia Blue pigment and beta-carotene.

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.

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:

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

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

9. A sugar-free syrup comprising a mixture of Gardenia Blue pigment and beta-carotene and a polyol.

10. The sugar-free syrup according to claim 9, wherein the polyol is selected from the group consisting of maltitol, xylitol, mannitol, sorbitol, isomalt, palatinose and mixtures thereof.

11. The sugar-free syrup according to claim 9 or 10, wherein the Gardenia Blue pigment has been obtained by a process comprising the following steps: ....
    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
    d) Optionally, purifying the Gardenia Blue pigment produced in step c).

12. A panned confection comprising:
    a) an edible product center, and
    b) an edible coating according to any one or more of claims 1 to 5.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2015/081265

A. CLASSIFICATION OF SUBJECT MATTER

A23L 1/275(2006.01)i; A23L 1/27(2006.01)i; A23G 3/00(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)

A23L; 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)

USTXT;CNKI;CNTXT;CNABS;DWPI: beta-carotene, gardenia blue, edible, confection, sugar, syrup, color, green

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011280942 A1 (SCHAD BEVERLY A ET AL.) 17 November 2011 (2011-11-17) the whole document	1-12
A	CN 102295788 A (BIOMARK CHINA INT LTD) 28 December 2011 (2011-12-28) the whole document	1-12
A	US 2010233252 A1 (QUALICAPS CO LTD) 16 September 2010 (2010-09-16) the whole document	1-12
A	WO 2011100643 A1 (SENSIENT COLORS INC ET AL.) 18 August 2011 (2011-08-18) the whole document	1-12
A	US 2014127299 A1 (NAZURA BIOHEALTH INC) 08 May 2014 (2014-05-08) the whole document	1-12
A	WO 2011112618 A1 (SENSIENT COLORS INC ET AL.) 15 September 2011 (2011-09-15) the whole document	1-12

☐ 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	Date of mailing of the international search report
24 February 2016	**14 March 2016**

Name and mailing address of the ISA/CN	Authorized officer
STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China**	**MA,Zhenpeng**
Facsimile No. **(86-10)62019451**	Telephone No. **(86-10)62084940**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2015/081265

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
US	2011280942	A1	17 November 2011	EP	2568973	A2	20 March 2013
				WO	2011143347	A3	23 February 2012
				WO	2011143347	A2	17 November 2011
CN	102295788	A	28 December 2011	None			
US	2010233252	A1	16 September 2010	EP	1983969	A1	29 October 2008
				JP	2009524573	A	02 July 2009
				WO	2007086586	A1	02 August 2007
				JP	5253162	B2	31 July 2013
				EP	1983969	A4	31 October 2012
WO	2011100643	A1	18 August 2011	EP	2533770	A4	17 December 2014
				JP	2013519686	A	30 May 2013
				EP	2533770	A1	19 December 2012
				US	2013115285	A1	09 May 2013
US	2014127299	A1	08 May 2014	WO	2014074749	A1	15 May 2014
				EP	2916828	A1	16 September 2015
WO	2011112618	A1	15 September 2011	EP	2544546	A4	15 October 2014
				US	2013095141	A1	18 April 2013
				EP	2544546	A1	16 January 2013