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(54) Title: NOVEL BETA-CAROTENE FORMULATIONS

(57) Abstract: The present invention is directed to a process for the manufacture of a formulation of β -carotene, wherein the β -carotene is embedded in a matrix of at least one modified food starch, and wherein the β -carotene in said formulation has a trans content $\geq 90\%$ and a median particle size of less than 400 nm, and the E1/1 of said formulation is > 800 , said process comprising the following steps: a) providing an aqueous suspension of β -carotene and at least one modified food starch (preferably OSA starch) to obtain an aqueous matrix; b) optionally wet media milling the matrix of step a) with milling beads, whereby the average diameter of the milling beads is ≥ 0.8 mm (preferably > 1.0 mm), to obtain a matrix of β -carotene, wherein the median particle size of the β -carotene is smaller than the median particle size of the β -carotene in the matrix of step a); c) wet media milling the matrix of step a) or step b) with milling beads, whereby the average diameter of the milling beads is in the range of from 0.1 to 0.8 mm (preferably 0.2 to 0.5 mm), to obtain a matrix of β -carotene with a median particle size of less than 400 nm; d) optionally removing the water of the matrix obtained in step c) to obtain a concentrated matrix; e) drying the concentrated matrix obtained in step c) or d) to obtain the formulation of β -carotene, wherein the β -carotene is embedded in the matrix of modified food starch, and wherein the β -carotene in said formulation has a trans content $\geq 90\%$ and a median particle size of less than 400 nm, and the E1/1 of said formulation is > 800 . The present invention is further directed to formulations obtained in such a process and to their use for coloring beverages and food, as well as to the beverages and food comprising such formulations.



Novel β -carotene formulations

β -carotene itself is not water-soluble. Thus, it has to be formulated to a water-soluble or water-dispersible formulation to use it e.g. for the coloration of beverages.

5

In most already known formulations β -carotene is embedded in a matrix of a hydrocolloid such as modified food starch to protect the β -carotene against degradation and oxidation. In the processes for manufacturing such formulations organic solvents are often used to get the β -carotene dissolved before emulsification into the aqueous matrix of the hydrocolloid.

10

There is a trend not to use such organic solvents any more. Thus, there is a need for a solvent-free process.

15 This need is fulfilled by the process of the present invention. Thus, the present invention is directed to a process for the manufacture of a formulation of β -carotene, wherein the β -carotene is embedded in a matrix of at least one modified food starch, and wherein the β -carotene in said formulation has a trans content $\geq 90\%$ and a median particle size of less than 400 nm (preferably a median particle size of less than 300 nm, even more preferably a median particle size of less than 200 nm), and the E1/1 of said formulation is > 800 (preferably the E1/1 of said formulation is > 1000), said process comprising the following steps:

20

a) providing an aqueous suspension of β -carotene and at least one modified food starch (preferably OSA starch) to obtain an aqueous matrix;

25

b) optionally wet media milling the matrix of step a) with milling beads, whereby the average diameter of the milling beads is ≥ 0.8 mm (preferably > 1.0 mm), to obtain a matrix of β -carotene, wherein the median particle size of the β -carotene is smaller than the median particle size of the β -carotene in the matrix of step a);

30

c) wet media milling the matrix of step a) or step b) with milling beads, whereby the average diameter of the milling beads is in the range of from 0.1 to 0.8 mm (preferably 0.2 to 0.5 mm), to obtain a matrix of β -carotene with a median particle size of less than 400 nm (preferably a median particle size of less than 300 nm, even more preferably a median particle size of less than 200 nm);

d) optionally removing the water of the matrix obtained in step c) to obtain a concentrated matrix;

e) drying the concentrated matrix obtained in step c) or d) to obtain the formulation of β -carotene, wherein the β -carotene is embedded in the matrix of modified food starch, and wherein the β -carotene in said formulation has a trans content $\geq 90\%$ and a median particle size of less than 400 nm (preferably a median particle size of less than 300 nm, even more preferably a median particle size of less than 200 nm), and the E1/1 of said formulation is > 800 (preferably the E1/1 of said formulation is > 1000).

Since steps b) and d) are optional, the present invention is therefore directed to

- I) a process comprising steps a), c) and d);
- II) a process comprising steps a), c) and e);
- III) a process comprising steps a), c), d) and e);
- IV) a process comprising steps a), b), c) and d);
- V) a process comprising steps a), b), c) and e); and to
- VI) a process comprising steps a), b), c), d) and e).

In preferred embodiments of the present invention the processes of the present invention consist only of these steps, and no additional steps are carried out.

Thus, the present invention is also directed to

- VII) a process consisting of steps a), c) and d);

- VIII) a process consisting of steps a), c) and e);
IX) a process consisting of steps a), c), d) and e);
X) a process consisting of steps a), b), c) and d);
XI) a process consisting of steps a), b), c) and e); and to
5 XII) a process consisting of steps a), b), c), d) and e).

The single steps are described in more detail below.

10 In contrast to the process of CN-A 103 406 079 non-ionic emulsifiers are not used in the process of the present invention.

Step a)

The β -carotene and the modified food starch are described in more detail below.

15 The amount of β -carotene in the matrix is chosen in such a way so that the amount of β -carotene in the formulation is in the range of from 0.1 to 10 weight-%, preferably wherein the amount of β -carotene in the formulation is in the range of from 2 to 6 weight-%, based on the total weight of the formulation.

20 β -carotene

Preferably β -carotene (1,3,3-Trimethyl-2-[3,7,12,16-tetramethyl-18-(2,6,6-trimethylcyclohex-1-en-1-yl)octadeca-1,3,5,7,9,11,13,15,17-nonaen-1-yl]cyclohex-1-ene) is used which has been synthetically manufactured. It is a mixture of cis- and trans-isomers. Surprisingly the amount of the trans-isomer did almost not change
25 during the process of the present invention, and is still >90% in the formulation obtained by the process of the present invention.

The formulation of the present invention has a color shade h is in the range of from 48 to 71 (preferably from 53 to 62, more preferably from 56 to 62) and a color value C*
30 of at least 30 (preferably in the range of from 31 to 52), when the color of such

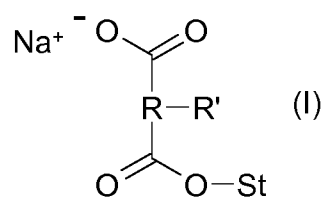
formulation is measured at the CIELAB color scale at a concentration of 5 ppm of β -carotene in water.

“Modified food starch”

- 5 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).
- 10 At least one modified food starch is preferably used to make a formulation of this invention, but it is possible to use a mixture of two or more different modified food starches in one formulation.

15 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

20 particularly preferred modified food starch of this invention has the following formula (I)



- 25 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 Co3, UNI-PURE, HYLON VII; from National Starch/Ingredion and Roquette Frères, respectively; from CereStar under the tradename C*EmCap or from Tate & Lyle.

Preferably no other hydrocolloid(s) than the modified food starch(es) is (are) present.

Step b)

Preferably the milling beads used in step b) are made of ceramic material.

In a further preferred embodiment of the present invention the filling of the milling beads in the mill in step b) is in the range of from 50 to 60%.

Preferably the temperature at which the milling in step b) takes place does not exceed 55° C.

Step c)

Preferably the milling beads used in step c) are made of ceramic material.

- 5 In a further preferred embodiment of the present invention the filling of the milling beads in the mill in step c) is in the range of from 50 to 60%.

Preferably the temperature at which the milling in step c) takes place does not exceed 55° C.

10

Step d)

The removal of the water may be achieved by any method known to the person skilled in the art. "Concentrated matrix" means that the amount of water in the matrix
15 obtained after having performed step d) is less than in the matrix of step c).

Step e)

The drying may be performed by spray-drying or by a so-called powder-catch process or by agglomeration.

20

Preferred embodiments of the process of the present invention

Preferably the process is carried out in the absence of an organic solvent. Such organic solvents which are preferably absent are e.g. chloroform, methylene chloride,
25 ethyl acetate, propyl acetate, hexane, heptane and/or mixtures thereof.

Preferably the process is carried out in the absence of an oil.

The formulation obtained by the process according to the present invention is also an object of the present invention, as well as the use of such formulation for coloring beverages or food.

- 5 Surprisingly the formulations obtained by the process according to the present invention have several advantages:
- The β -carotene embedded therein has a trans content $\geq 90\%$. This means that the trans content does almost not change during the process of the present invention.
 - The β -carotene embedded therein has a median particle size of less than 400 nm
10 (preferably less than 300 nm, more preferably less than 200 nm).
 - The E1/1 of said formulation is > 800 (preferably > 1000).
 - Furthermore, the formulations are color-stable and physically stable. Their shelf life is at least 3 months.
 - Furthermore, the β -carotene particles in such formulations do not only have
15 preferably a median particle size as given above, but their particle size distribution is quite narrow.

The formulation of the present invention has a color shade h is in the range of from 48 to 71 (preferably from 53 to 62, more preferably from 56 to 62) and a color value C^*
20 of at least 30 (preferably in the range of from 31 to 52), when the color of such formulation is measured at the CIELAB color scale at a concentration of 5 ppm of β -carotene in water.

25 Measurement of the particle size

In the context of the present invention the median particle size is the $x_{i,50}$ value.

Determination of E1/1

The color intensity E1/1 is the absorbance of a 1% solution and a thickness of 1 cm
30 and is calculated as follows: $E1/1 = (A_{max} - A_{650}) \cdot \text{dilution factor} / (\text{weight of sample} \cdot \text{content of product form in } \%)$.

“(Amax-A650)” means the value you get when you subtract the Adsorption value measured at 650 nm (“A650”) wavelength from the value (“Amax”) that was measured at the maximum Adsorption in the UV-Spectrophotometer.

5 “*” means “multiplied with”.

“dilution factor” = the factor by which the solution has been diluted.

“weight of sample” = the amount/weight of the formulation that was used in [g]

10 “content of product form in %” = “the amount of carotenoid in the suspension in %” which is from 2 to 6% in the present case.

Color measurements

Color measurements for the application in food are performed with a colorimeter (Hunter Lab Ultra Scan Pro) which can other than a spectrophotometer express color values according to the psychophysical perception of color by human eye.

20 Color measurements are carried out after CIE guidelines (Commission International d’Eclairage). Values can be expressed either as planar coordinates $L^*a^*b^*$ with L^* being the measuring value for lightness, with a^* being the value on the red-green-axis and with b^* being the value on the yellow-blue-axis.

Instrument settings:

- Color scale : CIE $L^*a^*b^*$ / $L^*C^*h^*$
- Light source definition: D65 daylight equivalent
- 25 • Geometry : Diffuse / 8°
- Wavelengths: scan 350 to 1050 nm in 5 nm optical resolution
- Sample measurement area diameter: 19 mm (large)
- Calibration mode: Transmission/ white tile

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

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

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

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

The color difference DE^* is calculated using the following equation:

10

$$DE^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

whereby L = lightness, a = red value, and b = yellow value

$\Delta L^* = L_x^* - L_0^*$; 0 = initial value; x = time of measuring

$\Delta a^* = a_x^* - a_0^*$; 0 = initial value; x = time of measuring

15 $\Delta b^* = b_x^* - b_0^*$; 0 = initial value; x = time of measuring

For a good color stability, DE^* should be lower than 10 ($DE^* < 10$); this means that the color difference is acceptable and at $DE^* < 3$ cannot be seen by naked eyes, i.e. without the use of an apparatus such as a colorimeter.

20

Physical stability

Physical stability is measured by human eye according to an evaluation matrix.

Parameter recorded for soft drink beverages are:

- Ring formation / Neck ring in bottles in score 6 to 1 with "6" representing "no ring", and "1" representing "very strong ring".
- Surface particles in score 6 to 1 with "6" representing "no particles / no covering" and "1" representing "more than half of surface covered with particles / more than two third of surface covered with film other than particles".

- Sediment on the bottom of packaging as fine film, individual particles or ring-formation in score 6 to 1 with “6” representing “either no particles, no film or no ring” and “1” representing “either more than half of bottom covered with particles, bottom covered with strong film or very strong ring visible”.

5

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

Examples

10 Example 1: Preparation of β -carotene suspensions

The β -carotene is suspended in water containing modified food starch. The solid content is set to ca. 50%, which results in a suspension with medium viscosity (around 300 mPa s). Three different suspensions are prepared with increasing β -carotene contents, namely 2%, 4% and 6%.

15

Example 2: Particle size reduction through wet-milling

Prior to each milling experiment the β -carotene suspension is stirred for 15 minutes at 1000 rpm to get a homogeneous mixture. After redispersion, a preliminary milling is conducted in pendulum mode with a grinding media size of 0.8 mm. The filling ratio
20 varies from 50 to 60%. Then a milling step is performed by using a grinding media size of 0.2 mm in circuit mode.

Measurement of the particle size

During all milling experiments samples were taken at 5, 15, 30, 60, 90 and 120
25 minutes to analyze the particle size reduction. All these samples were homogenized for about 30 seconds and diluted with purified water by a factor of 100 to get a measurable suspension. Before the measurement, the samples were mixed for another 30 seconds. The measuring parameters on the Malvern ZetaSizer Nano ZS were adjusted for β -carotene by specifying the corresponding refractive index (1.57
30 [SCBT.de]) and an absorption value of 0.3. Three consecutive measurements were

made and the mean value was taken as the measured particle size respectively particle size distribution.

5 Example beverage application

Recipe for soft drink preparation

Ingredients	Amount (g)
Sugar syrup 64° Brix	156.2
Citric acid 50% solution	5
Potassium sorbate	0.2
Ascorbic acid fine powder	0.2
Apricot flavour	0.2
β -carotene as 1% stock solution	6
Water	To 1000ml

The soft drinks were prepared as follows:

- 10 Potassium sorbate 1) was dissolved in water, the other ingredients 2) were added one after the other while the mixture was gently stirred. Then the resulting soft drink syrup was diluted with drink water 3) in such an amount to result in 1000 ml of the soft drink. The pH of the soft drinks was in the range of 2.8 to 3.5.

- 15 The soft drinks were then filled in glass bottles and the bottles sealed with a metallic cap. Some of these bottles were pasteurized and some not. A tunnel pasteurizer from Mile was used for pasteurization with a holding temperature of 80°C for 1 minute at a core of the bottle.

- 20 The bottles were stored at room temperature (temperature in the range of 18 to 27°C) and under light exposure 12 hours per day with 800 Lux. Color measurements were performed directly after beverage preparation (time = 0), as well as after a storage time of 2 weeks, 30 days, 60 days and 90 days.

All samples showed a good color stability as defined above.

Claims

1. A process for the manufacture of a formulation of β -carotene, wherein the β -carotene is embedded in a matrix of at least one modified food starch, and wherein the β -carotene in said formulation has a trans content $\geq 90\%$ and a median particle size of less than 400 nm, and the E1/1 of said formulation is > 800 , said process comprising the following steps:
- 5 a) providing an aqueous suspension of β -carotene and at least one modified food starch (preferably OSA starch) to obtain an aqueous matrix;
- 10 b) optionally wet media milling the matrix of step a) with milling beads, whereby the average diameter of the milling beads is ≥ 0.8 mm (preferably > 1.0 mm), to obtain a matrix of β -carotene, wherein the median particle size of the β -carotene is smaller
- 15 than the median particle size of the β -carotene in the matrix of step a);
- 20 c) wet media milling the matrix of step a) or step b) with milling beads, whereby the average diameter of the milling beads is in the range of from 0.1 to 0.8 mm (preferably 0.2 to 0.5 mm), to obtain a matrix of β -carotene with a median particle size of less than 400 nm;
- 25 d) optionally removing the water of the matrix obtained in step c) to obtain a concentrated matrix;
- 25 e) drying the concentrated matrix obtained in step c) or d) to obtain the formulation of β -carotene, wherein the β -carotene is embedded in the matrix of modified food starch, and wherein the β -carotene in said formulation has a trans content $\geq 90\%$ and a median particle size of less than 400 nm, and the E1/1 of said formulation is > 800 .

2. The process according to claim 1, whereby the process is carried out in the absence of an organic solvent.
3. The process according to claim 1, whereby the process is carried out in the absence
5 of an oil.
4. The process according to one or more of the preceding claims, wherein the amount of β -carotene in the formulation is in the range of from 0.1 to 10 weight-%, preferably wherein the amount of β -carotene in the formulation is in the range of from 2 to 6
10 weight-%, based on the total weight of the formulation.
5. The process according to one or more of the preceding claims, wherein the milling beads used in step b) and/or c) are made of ceramic material.
- 15 6. The process according to one or more of the preceding claims, wherein the filling of the milling beads in the mill in step b) and/or c) is in the range of from 50 to 60%.
7. The process according to one or more of the preceding claims, wherein the temperature at which the milling in step b) and/or step c) takes place does not
20 exceed 55° C.
8. A formulation obtained by the process according to any one or more of claims 1-7.
9. A formulation of β -carotene, wherein the β -carotene is embedded in a matrix of at
25 least one modified food starch, and wherein the β -carotene in said formulation has a trans content $\geq 90\%$ and a median particle size of less than 400 nm, and the E1/1 of said formulation is > 800 .
10. The formulation according to claim 8 and/or 9, wherein the color shade h is in the
30 range of from 48 to 71 (preferably from 53 to 62, more preferably from 56 to 62) and the color value C^* is at least 30 (preferably in the range of from 31 to 52), when the

color of such formulation is measured at the CIELAB color scale at a concentration of 5 ppm of β -carotene in water.

5 11. Use of the formulation according to claim 8, 9 and/or 10 for coloring beverages or food.

12. Beverages comprising a formulation according to claim 8, 9 and/or 10.

13. Food comprising a formulation according to claim 8, 9 and/or 10.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/064380

A. CLASSIFICATION OF SUBJECT MATTER

INV. A23L33/105 A23L2/58 B02C17/00 C07C403/24 C08B30/00
C08B31/00 C12P23/00 C08L3/02 A23P10/30 A23P20/10
A23L29/212 A23L29/30 A23L5/44

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 B02C C07C C08B C12P C08L C08J A23P

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, FSTA, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 103 406 079 A (INNOBIO LTD) 27 November 2013 (2013-11-27) paragraph [0023] - paragraph [0042]; claims 1, 6, 8; example 2 -----	1-13
X	EP 2 644 041 A1 (DSM IP ASSETS BV [NL]) 2 October 2013 (2013-10-02) paragraph [0001] - paragraph [0072]; claims 1, 2, 8, 21; examples 1-16 -----	1-13
X	EP 1 300 394 A1 (VITATENE SA [ES]; WILD GMBH & CO KG RUDOLF [DE]) 9 April 2003 (2003-04-09) paragraph [0001] - paragraph [0023]; claim 18 ----- -/-	1-13



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"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

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Date of the actual completion of the international search

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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.
X	EP 1 964 479 A1 (DSM IP ASSETS BV [NL]) 3 September 2008 (2008-09-03) tables 9, 10	8-10, 12, 13
X	----- US 2008/207775 A1 (MUSAEUS NINA [DK] ET AL) 28 August 2008 (2008-08-28) paragraph [0084]; claim 21 -----	8-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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