Mix organic acid with calcium source

Add at least one metal source

Dry composition

(57) Abrégé/Abstract:
The present invention concerns a stable calcium composition, a process for its preparation and its use for enriching food and beverages. The calcium composition comprises a calcium source, a citrate and a metal source selected from alkali and/or alkaline source.
Title: CALCIUM ENRICHMENT COMPOSITIONS METHOD OF PRODUCTION THEREOF AND USE

Abstract: The present invention concerns a stable calcium composition, a process for its preparation and its use for enriching food and beverages. The calcium composition comprises a calcium source, a citrate and a metal source selected from alkali and/or alkaline source.
CALCIUM ENRICHMENT COMPOSITIONS METHOD OF PRODUCTION THEREOF AND USE

FIELD OF THE INVENTION

This invention relates to calcium containing compositions, process for their production and their use. More particularly, this invention is directed to stable calcium-containing compositions for use as food and beverage additives.

BACKGROUND OF THE INVENTION

Mineral and vitamin supplements are often used to fortify the composition of food and beverages, both for human and veterinary use. For example, US 4,772,467 to Pak et al., discloses the use of citrate based calcium sources for increasing the bioavailability of the calcium. US Patent No. 4,786,518 to Nakel et al., describes nutritional supplements comprising iron-sugar complexes. US Patent 4,992,282 to Mehdansho et al. describes stable nutritional vitamin and mineral supplemented beverages.

It is known that the recommended daily allowance (RDA) of calcium, for example, is around 1200 mg per day for an adult. Most of the dietary calcium in a western diet is from cow milk and other dairy products. The calcium content of cow milk is typically in the range of 900 – 1100 mg per liter, such that one liter almost provides the RDA. Cow milk substitutes such as soy milk or rice milk provide much less calcium than cow milk and almost all the Calcium is added artificially.

Calcium supplements find wide applications as food and beverage supplements. They are used, inter alia, to compensate calcium loss from the human body, as is exhibited in osteoporosis. For example, US Patent No. 4,949,283 to Mehdansho et al. discloses iron-calcium mineral supplements with enhanced bioavailability. US Patent No. 5,445,837 to Burkes et al., discloses as sweetener supplement fortified with a concentrated bioavalible calcium source and process for making them. US Patent No. 5,486,506 to Andon discloses a concentrated bioavalible calcium source. US Patent No. 6,828,130 to Chatterjee et al., discloses methods for production of gluconate salts. US
Patent No. 6,887,897 to Walsdorf, Sr., et al. discloses calcium glutarate supplements and phosphorus binders.

 Numerous other relevant patents in the art of food and beverage supplements include: US 4,214,996; 4,351,735; 4,551,432; 4,737,375; 4,851,221; 4,895,980, 4,985,593; 5,204,134; 5,213,134; 5,213,838; 5,219,889; 5,928,691; 6,287,607; 6,248,376 and 6,599,544.

 Buddemeyer et al., disclose phosphate containing compositions for use as additives to milk in US 6,248,376 and US 6,599,544.

 SUMMARY OF THE INVENTION

 The present invention is directed to edible calcium comprising compositions that are stable in food and beverages. The calcium comprising compositions are stable in beverages, or in their concentrates, and may not separate out of the liquid phase even under long storage periods. The calcium comprising composition of the present invention may be palatable and may not affect the organoleptic properties of the beverage or beverage concentrate to which it is introduced and thus can serve as an effective calcium supplement (fortifier) for beverages and solid food.

 Thus, in one aspect the present invention provides a dry calcium rich composition comprising:

 (i) at lease one source of calcium;
 (ii) at least one source of metal that is an alkaline metal other than calcium or an alkali metal; and
 (iii) at least one source of citrate;

 wherein the composition has a bulk density of less than 0.4-0.5 g/cm³, comprises at least 15% (wt/wt) calcium and at least 66% (wt/wt) of citrate on dry weight basis. More preferably the composition comprises 15% to 20% (wt/wt) calcium and at least 71% (wt/wt) citrate on a dry basis.

 The composition may further comprise 7-10% crystalline water. It may further comprise stabilizers, coloring agents or emulsifiers.

 In particular, the calcium rich composition of the invention may be used to enrich beverages with calcium, especially in milk, milk-like beverages and naturally or
artificially fortified protein containing beverages. It may be either soluble in the beverage or exist as a suspended addition. In some embodiments, the calcium enriched composition introduced into a beverage is stable for a period of at least 10 to 70 days wherein less than 5% (wt/wt) of the composition sediments out of the beverage. It should be noted that "stable" relates to the fact that the calcium enriched composition remains within the liquid phase substantially without sedimenting out. By "substantially without" it is meant that less than 5% of the composition is precipitated. Remaining within the liquid means at least one of remaining suspended, remaining dissolved and remaining bound to a suspended solid or liquid.

In some embodiments, the calcium source is calcium hydroxide, calcium oxide, calcium carbonate, calcium propionate, calcium gluconate, calcium citrate, calcium stearate, calcium fumarate, or calcium glycerophosphate.

In some embodiments, the citrate is citric acid, citric acid monohydrate, citric acid mono-, di- or tri-sodium salt, citric acid mono-, di- or tri-potassium salt or ammonium citrate.

In some embodiments, the at least one metal source is a source of sodium, a source of potassium, a source of magnesium or their mixtures. In some embodiments, the potassium source is selected from potassium hydroxide, potassium citrate, potassium carbonate, potassium bicarbonate or their mixtures. In some embodiments, the magnesium source is selected from magnesium oxide, magnesium hydroxide, magnesium carbonate, magnesium citrate or their mixtures. In some embodiments, the sodium source is selected from sodium hydroxide, sodium citrate, sodium carbonate, sodium bicarbonate or their mixtures.

Preferably, the calcium enriched dry composition of the present invention comprises a molar ratio of 3-4.5 citrate; 4-6 calcium; and 2-3 of at least one metal source. Such a preferred composition may comprise: (i) a molar ratio of citrate 3-4.5: calcium 4-6: potassium 2-3: and magnesium 0-1; (ii) a molar ratio of citrate 4: potassium 2: calcium 5; (iii) a molar ratio of citrate 3-4.5: calcium 4-6: potassium 2-3: and sodium 0-1.

In another aspect, the invention provides a method for producing a dried calcium-rich composition comprising:
(i) mixing at least one source of citrate with at least one source of calcium and at least one metal source selected from:
   a) an alkaline earth metal source; and
   b) an alkali metal source;
   in a molar ratio of at least three moles citrate, at least five moles of calcium and at least two moles of the at least one metal source so as to produce an organic calcium solution; and

(ii) drying the organic calcium solution so as to produce the dried calcium-rich composition, wherein said composition comprises at least 66% citrate on a dry weight basis, and wherein said composition comprises at least 15% calcium on a dry weight basis.

In other aspects, the invention provides a food or nutritional product comprising the calcium enriched composition. The nutritional product may be a beverage or beverage concentrate comprising the calcium enriched composition. In particular embodiments, the beverages are milk based beverages that may be fortified with proteins, vitamins, minerals or their mixtures. Non-limiting examples of beverages are selected from soy milk, cow milk, camel milk, goat milk, or their mixtures. Such beverages may further comprise additional edible supplements selected from cocoa, vanilla, fruit or vegetable concentrates or flavorings.

**BRIEF DESCRIPTION OF THE DRAWINGS**

In order to understand the invention and to see how it may be carried out in practice, embodiments will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

**Fig. 1** is a simplified flowchart illustrating a process for producing a dried calcium-rich composition according to a preferred embodiment of the present invention;

**Fig. 2** is a simplified flowchart illustrating further details of one embodiment of step 110 of Fig. 1;

**Fig 3** is a simplified flowchart illustrating a process for producing a dried calcium-rich composition according to a preferred embodiment of the present invention;
Fig. 4 is a simplified flowchart illustrating a process for supplementing a food or beverage with the dried calcium-rich composition according to a preferred embodiment of the present invention; and

Fig. 5 is another simplified flowchart illustrating a process for supplementing a food or beverage with the dried calcium-rich composition according to a preferred embodiment of the present invention.
DETAILED DESCRIPTION OF EMBODIMENTS

The present invention is thus directed to calcium comprising compositions, which are stable in food and beverages and in food and beverage supplements. Preferably the compositions are suitable for use in milk, soy milk and other "milk-like", "milk-containing", protein containing beverages or their mixtures. Despite the large number of supplements currently available and known in the art, many of them are unstable and precipitate out of solution over time. The products of the present invention may be used to meet the demand in the market for stable sources of calcium, which are suitable for adding to foods and beverages. The products of the present invention are used as supplements and do not affect the organoleptic properties or the taste of the food or beverage to which they are added. The calcium products of the present invention are both stable and do not typically precipitate during the storage of the food/beverage even after storage periods of about 70-80 days.

The present invention relates in particular to stable dried compositions of organic calcium, in the form of calcium citrate with at least one other additional metal, to methods for the preparation of these compositions and their use as calcium supplements. The products of this invention may be used either directly for enhancing uptake of calcium or as an additive in various food and beverages to fortify these food products with calcium. The compositions are stable in beverages and in food, to which they added.

The compositions of the present invention exhibit high bioavailability. The compositions of the present invention are stable in sterilization and pasteurization processes known in the art of food and beverage processing. The composition of the present invention does not require the co-addition of hydrocolloids in order to retain the calcium in a stable suspension.

Reference is now made to **Fig. 1**, which is a simplified flowchart illustrating a process for producing a dried calcium-rich composition according to a preferred embodiment of the present invention.

In a first mixing step **110**, an organic acid solution **102**, being a citrate solution is mixed with a calcium source **104**. The citrate solution which is citric acid or its salts, is typically in a concentration range of 0.1 to 0.5 M. Non limiting sources of calcium according to the present invention are selected from the group of calcium hydroxide, calcium oxide, calcium carbonate, calcium propionate, calcium gluconate, calcium
citrate, calcium stearate, calcium fumarate, calcium glycerophosphate. The calcium source 104 is provided to produce a solution with molar ratio of Calcium to Citrate typically in the range of 1.1 – 1.3. Typically this step is performed in a standard mixed vessel well known in the art. This mixing step 110 typically takes up to 30 minutes. In this step 110, the vessel is typically cooled to a set temperature below 25°C. Cooling jackets known in the art, may be employed on a large scale, or the vessel may be at least partially immersed in a water bath on the small scale, as is known in the art. In the present invention different chillers were used (such as CH10TR nameplate number 30089, Unique, Nehalim, Israel or CC230, Huber High Precision Thermoregulation, Offenburg, Germany)

Typically, the citrate solution 102 is obtained commercially. Alternatively, it may be prepared in situ as is exemplified in Fig. 2 herein below.

Typically, solution 106 comprises 4 to 25 % total dissolved solids (TDS). In some embodiments, there are 5 to 10 % TDS in solution.

Solution 106 and/or solution 126 (described hereinbelow) typically has a pH value in the range of 4.5 to 12, and more preferably from 5 to 10.

In an addition step 120, at least one metal source 124 selected from an alkaline earth metal source and an alkali metal source is added to calcium citrate solution 106 to form a calcium metal citrate solution 126. This may be performed in the same or different vessel to that of step 110. The at least one metal source is selected from at least one potassium source, at least one magnesium source, at least one sodium source or their mixtures. Non-limiting examples of the potassium source are potassium hydroxide, potassium citrate, potassium carbonate and potassium bicarbonate. Typically the potassium salt is added in to produce the molar ratio of potassium to citrate in a range 0.6 – 0.8. Non-limiting examples of the magnesium source are magnesium oxide, magnesium hydroxide magnesium citrate, magnesium carbonate. Typically the magnesium salt is added in suitable concentration to produce the molar ratio of Magnesium and Citrate in range 0.1 to 0.25.

In the drying step 130, solution 126 is dried and liquid 138 is removed there from to form a dry calcium metal citrate composition 136. Step 130 typically drying solution 126 into a powder using a spray drying or freeze drying process in a dryer APV PSD52 (APV Nordic Anhydro, Silkeborg, Denmark) using the inlet air with temperature from 190 up to 350°C as is known in the art. Excess liquid 138 is removed
from the solution until a solid phase forms. The solid phase may be in the form of a powder, flakes, granules or other solid form. The resultant composition 136 may then be suitably stored and/or packaged (not shown). The resultant composition typically has a bulk density of less than 0.6 g/cm³, more typically, less than 0.5 g/cm³.

Dry calcium metal citrate composition 136 typically has a composition as is shown in Table 1. It should be noted that all the examples herein of the composition produced comprises 7-10% adsorbed (crystalline) water.

Table 1: Typical Composition of a Calcium Metal Citrate Composition on a Dry Weight Basis*

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>RELATIVE MOLAR RATIO</th>
<th>PERCENT OF DRY COMPOSITION [WT/WT %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CITRATE</td>
<td>1</td>
<td>63-75</td>
</tr>
<tr>
<td>CALCIUM</td>
<td>0.8 -2</td>
<td>13-18</td>
</tr>
<tr>
<td>POTASSIUM</td>
<td>0.4 -1</td>
<td>6 – 10</td>
</tr>
<tr>
<td>MAGNESIUM</td>
<td>0.03 – 0.3</td>
<td>0.5 – 1.5</td>
</tr>
</tbody>
</table>

* it should be noted that the "dry weight" was calculated excluding up to 10% adsorbed water in the product.

Reference is now made to Fig. 2, which is a simplified flowchart 200 illustrating further details of one embodiment of step 110 of Fig. 1.

In a mixing step 210, water 202, such as deionized water, is mixed with a citrate containing solid or solution 204. Citrate containing solid or solution 204 is selected from citric acid (Sigma Aldrich Corporation, St. Louis, Missouri, USA cat. Number C0759, C7129 or cat. Number C0706, C1909), sodium citrate (Sigma Aldrich Corporation, St. Louis, Missouri, USA cat. Number C0759, C7129 or cat. Number S4641) and potassium citrate (Sigma Aldrich Corporation, St. Louis, Missouri, USA cat. Number C0759, C7129 or cat. Number C8385). Typically suitable amount of citric acid or a citrate salt is added to provide a concentration of citrate ions in range up to 0.5 moles per liter of water. Water 202 and citrate containing solid or solution 204 are typically mixed at room temperature in any kind of well known in the art mixed vessel. This mixing step 210 typically takes up to 1 hour to provide a full dissolution. In this step 210, the vessel is typically cooled to a set temperature ranging from 5-25°C.
Cooling jackets known in the art, may be employed on a large scale, or the vessel may be at least partially immersed in a water bath on the small scale, as is known in the art.

The resultant citrate solution 206, typically comprises 0.1 -0.5 mol per liter of citrate.

In an addition step 220, a suitable source of calcium 224 is added to the citrate solution to form an organic calcium citrate solution 226. Typically this step is performed in a standard well known in the art mixed vessel. This step 220 typically takes up to 30 minutes while mixed. In this step 110, the vessel is typically cooled to a set temperature ranging below 25°C. Cooling jackets known in the art, may be employed on a large scale, or the vessel may be at least partially immersed in a water bath on the small scale, as is known in the art.

The calcium source may be selected from, but is not limited to, calcium citrate; calcium oxide, calcium hydroxide and calcium carbonate (of Sigma Aldrich Corporation, St. Louis, Missouri, USA cat. Numbers C2178, C4830, C7887, or Fluka Buchs, Switzerland, cat. number 21118, cat. number 21120). The calcium source is provided to produce a molar ratio of calcium to citrate ion in range 1.1 -1.3 in solution 226.

Reference is now made to Fig 3, which is a simplified flowchart 300 illustrating a process for producing a dried calcium-rich composition according to a preferred embodiment of the present invention.

In a mixing step 310, citric acid 304 (Gadot Biochemical Industries, Ltd., Haifa, Israel) is mixed in water 302, typically deionized water so as to produce a citric acid solution 306 of 0.1 to 0.5 moles per liter.

In a metal addition step 320, at least one source of metal 324 is added to the citric acid solution to form a metal rich citric acid solution 326. Typically, at least one source of potassium is added. The potassium source is selected from, but not limited to potassium hydroxide, potassium citrate, potassium carbonate and potassium bicarbonate (Sigma Aldrich Corporation, St. Louis, Missouri, USA Cat. Numbers P9144, P5833, P4379, P6037, C8385, P5958, P1767, 60025, 60028). Typically the potassium salt is added in to produce the molar ratio of potassium to citrate in a range 0.6 – 0.8. In some embodiments, Sodium was used instead of potassium. In some embodiments, ammonium was used instead of potassium or sodium.
In some embodiments, the magnesium source is selected from, but not limited to, magnesium oxide, magnesium hydroxide, magnesium citrate, magnesium carbonate, (Sigma Aldrich Corporation, St. Louis, Missouri, USA Cat. Numbers M7179, M5671, M5421, M8511, 30.77-2, M7861, and Merck & Co, Inc, Whitehouse Station, NJ, USA Cat. Numbers 105904). Typically the magnesium salt is added in a suitable concentration to produce the molar ratio of magnesium and citrate in range 0.1 to 0.25. In some embodiments, no magnesium is added.

In some embodiments, step 330 is performed before step 320. Other variations on the flowcharts of Figs. 1-3 also fall within the scope of the present invention.

In a second addition step 330, a calcium source 334 is added to solution 326 so as to form a calcium metal citrate solution 336.

The calcium source 334 may be selected from, but is not limited to, calcium citrate; calcium oxide, calcium hydroxide and calcium carbonate (Sigma Aldrich Corporation, St. Louis, Missouri, USA cat. Numbers C2178, C4830, C7887, or Fluka Buchs, Switzerland, cat. number 21118, cat. number 21120). The calcium source is provided to produce solution 336 with molar ratio of Calcium to Citrate in range 1.1 – 1.3. The process conditions in this step and in step 330 may be similar to, identical to or different from those of step 120 of Fig. 1.

In a drying step 340, solution 336 is dried, liquid 348 is removed there from to form a dry calcium metal citrate composition 346. Step 340 typically dries solution 336 into a powder using a spray drying or freeze drying process in a dryer (APV PSD52, APV Nordic Anhydro, Silkeborg, Denmark) using the inlet air with temperature from 190 up to 350 Degrees Celsius as is known in the art. Excess liquid 348 is removed from the solution until a solid phase forms. The solid phase may be in the form of a powder, flakes, granules or other solid form. The resultant composition 346 may then be suitably stored and/or packaged (not shown). Typically, the composition obtained has a bulk density of less than 0.5 g/cm³.

Reference is now made to Fig. 4, which is a simplified flowchart 400 illustrating a process for supplementing a food or beverage with the dried calcium-rich composition according to a preferred embodiment of the present invention.

In a mixing step 410, a dried calcium metal citrate composition 402 is mixed with a food or beverage 404 to form calcium enriched beverage/food 416. Composition 402 may be similar or identical to composition 136 or composition 346. The food may
be in a liquid or solid state. The food may be exemplified by, but not limited to a cheese, yoghurt, cream, spread, cereal, or chocolate.

The beverage may be a natural based beverage or a non-natural based beverage. Non-limiting examples of beverages according to the present invention are fruit or vegetable based beverages, milk-based beverages, that may further comprise flavoring additives such as proteins, minerals or vitamins. Thus these may be milk, milkshake, nectars, or chocolate milk. The milk may be selected from, but not limited to, soy milk, reconstituted milk formula, goat milk, sheep milk, camel milk, substitute milk, cow milk, oat milk and human milk, or may be any mixture thereof, or beverages based on them.

The ratio of composition 402 added to a liquid food/beverage 404 is typically suitable to provide a Calcium concentration up to 1.5 RDA of Calcium per liter. Calcium enriched beverage/food 416 typically comprises 1200 mg/l calcium.

Alternatively, calcium enriched beverage/food 404 is in a solid form and is mixed with composition 402 in any kind of well known in the art mixed vessels for about 15 minutes or till the homogeneous dispersion is obtained.

In an optional storage step 420, a liquid calcium enriched beverage/food 416 is stored for a period of few months at ambient conditions or during refrigeration. The properties of stored calcium enriched beverage/food 426 are compared to those of calcium enriched beverage/food 416. Typically, the composition is stable in the liquid and less than 10 % of the calcium precipitates out of the liquid. In accordance with the stability of the added calcium fortifying composition, the initial calcium concentration introduced into the food/beverage 426 is maintained, where it preferably comprises at least 1200 mg/L of calcium.

In an optional dilution step 430, stored calcium enriched beverage/food 426 is diluted with water 434 to form a ready-to-use calcium enriched beverage/food product 436. For example, beverage/food 426 may be in a concentrated form such as a milk powder, baby milk liquid/solid formula, cream or concentrate, which may be diluted for use with water according to the relevant ratio or instructions provided therewith.

In some other embodiments, food product 404 is pre-dried and is reconstituted in step 430. Non-limiting examples are dried mashed potatoes, dried packet soups, milk powder, meat, yeast and protein extracts and "heat and eat" meals.
Reference is now made to **Fig. 5**, which is a simplified flowchart **500** illustrating a process for supplementing a food or beverage with the dried calcium-rich composition according to a preferred embodiment of the present invention.
In a mixing step 510, a dried calcium rich composition 502 is mixed with water 504 to form a wet calcium rich composition 516. Composition 502 may be similar or identical to composition 136 or composition 346. Step 510 is performed in a any kind of well known in the art mixing vessel until an homogeneous suspension is obtained.

Typically about 100 g of composition 502 is added per liter of water such that the wet calcium rich composition comprises about 15 g calcium/l.

In an addition step 520, wet composition 516 is added to food/beverage 524 to form calcium-enriched food/beverage 526. The calcium-enriched food/beverage typically comprises 1200mg calcium/l.

Step 520 is performed in any kind of well known in the art mixing for about 15 min or until the homogeneous suspension obtained.

In an optional storage step 530, calcium-enriched food/beverage 526 is stored for a period of at least a few month at ambient conditions or at refrigeration. The properties of stored calcium enriched beverage/food 536 are compared to those of calcium enriched beverage/food 526. Typically, less than 10 % of the calcium precipitates out of the liquid. In some embodiments less than 5 % of the calcium precipitates out of the liquid such that stored beverage/food 536 comprises at least 1200 mg/l calcium.

**Example 1**

1840 ml of deionized water were placed in a 5 L beaker and the temperature kept in the range of 5-25°C. While stirring, 66.5g citric acid was added followed by 2.5g of MgO. Thereafter, 23.3gr CaO were added. Finally, 13 g KOH was added. The mixture was well stirred, dried (as described with reference to the flowcharts hereinabove). The dry product obtained had properties in the range of those described in Table 1 hereinabove.

**Example 2**

920 ml of deionized water were placed in a 5 L beaker and the temperature kept in the range of 5-25°C. While stirring, 36.5 g citric acid was added followed by 13.6g of CaO. Finally, 6.5 g KOH were added. The mixture was well stirred and dried (as
described with reference to the flowcharts hereinabove). The dry product obtained had properties in the range of those described in Table 1 hereinabove.

**Example 3**

920 ml of deionized water were placed in a 5 L beaker and the temperature kept in the range of 5-25°C. While stirring, 66.5g citric acid was added followed by 2.5g of MgO. Thereafter were added 23.3gr CaO. Finally, there were added 13 gr KOH. The mixture was well stirred, dried (as described with reference to the flowcharts hereinabove). The dry product obtained had properties in the range of those described in Table 1 hereinabove.

**Example 4**

To 1000 ml of cow milk 3 % fat (Tnuva, Rehovot, Israel), 6.7 grams of composition, prepared as described in Example 1, was added while stirring with well known in the art laboratory magnetic stirrer. The initial concentration of calcium was tested and found 2230 mg/liter. After storing for 6 days at 4 Degrees Celsius, the concentration of Calcium in the upper layer was tested again and found to be 2225 mg/liter.

**Example 5**

To 1000 ml of natural soy milk (Alpro N.V., Wevelgem, Belgium), 6.7 g of composition (prepared as described in example 1) was added while stirred with a laboratory magnetic stirrer to form an enriched soy milk. The initial concentration of calcium in the enriched soy milk was tested and found 1327 mg/liter. After storing for 6 days at 4 Degrees Celsius, the concentration of calcium of the enriched soy milk was tested again and found 1325 mg/liter.

**Example 6**

1840 ml of deionized water were placed in a 5 L beaker and the temperature kept in the range of 5-25°C. While stirring, 66.5g citric acid were added followed by 2.5g of MgO. Thereafter were added 23.3gr CaO. Finally, there were added 7.7 gr NaOH. The mixture was well stirred, dried (as described with reference to the flowcharts hereinabove).
Example 7
To 1000 ml of natural soy milk (Alpro N.V., Wevelgem, Belgium) 6.7 g of composition (prepared as described in Example 6 hereinabove) was added under stirring with a laboratory magnetic stirrer so as to form enriched soy milk. The initial concentration of calcium was tested in the enriched soy milk and found to be 1305 mg/liter. After storing for 6 days at 4 Degrees Celsius, the concentration of Calcium in the enriched soy milk was tested again and found to be 1306 mg/liter.

Example 8
To 1000 ml of natural soy milk (Alpro N.V., Wevelgem, Belgium), 6.7 g of composition (prepared as described in Example 1 hereinabove) was added under stirring with a laboratory magnetic stirrer to form enriched soy milk. In addition, 0.2 g of Cappa Karragenan (Sigma Aldrich Corporation, St. Louis, Missouri, USA cat. Number C1263) was added. The initial concentration of calcium in the enriched soy milk was tested and found to be 1396.7 mg/liter. After storing for 6 days at 4 Degrees Celsius, the concentration of calcium in the enriched soy milk was tested again and found 1401.1 mg/liter.

Example 9
To 1000 ml of natural soy milk (Alpro N.V., Wevelgem, Belgium) 6.7 g of composition (prepared as described in Example 1 hereinabove) was added while stirred with a laboratory magnetic stirrer to form enriched soy milk. The enriched soy milk was passed through homogenizer (APV PSD52, APV Nordic Anhydro, Silkeborg, Denmark). Thereafter, the initial concentration of calcium was tested and found 1446.6 mg/liter. After storing for 6 days at 4 Degrees Celsius, the concentration of calcium of the enriched soy milk was tested again and found 1432.3 mg/liter.

Example 10
The material was prepared as described in Example 1 hereinabove, but the aqueous suspension was stored for 10 hours prior to the drying step. Thereafter, the material was dried as described with reference to the flowcharts hereinabove. The dry product obtained had properties in the range of those described in Table 1 hereinabove.
Example 11

To 1000 ml of natural soy milk (Alpro N.V., Wevelgem, Belgium) 6.7 g of composition (prepared as described in Example 10) was added under stirring with a the art laboratory magnetic stirrer and an enriched soy milk product was formed. The initial concentration of calcium in the product was tested and found 1267 mg/liter. After storing for six days at 4 Degrees Celsius, the concentration of calcium in the product was tested again and found 1266 mg/liter.

Example 12

To 1000 ml of natural soy milk (Alpro N.V., Wevelgem, Belgium) 6.7 g of composition (prepared as described in Example 1 hereinabove) was added under stirring employing a laboratory magnetic stirrer to form a calcium-enriched composition. The calcium-enriched composition underwent ultra-high temperature (UHT) treatment (4 sec at 140°C) as is known in the art. The initial concentration of calcium in the calcium-enriched composition was tested and found 905 mg/liter. After storing for 7 days at 4 Degrees Celsius, the concentration of calcium in the calcium-enriched composition was tested again and found 906 mg/liter. After storing for another 7 days at 4 Degrees Celsius, the concentration of calcium in the calcium-enriched composition was tested again and found 905.5 mg/liter. After retention of 70 days at 4 Degrees Celsius, the concentration of calcium in the calcium-enriched composition was tested again and found 905 mg/liter.

Example 13

1840 ml of deionized water were placed in a 5 L beaker and the temperature kept in the range of 5-25°C. While stirring, 66.5g citric acid were added followed by 2.5g of MgO. Thereafter were added 23.3g CaO. Finally, there were added 8.12 gr NH₄OH. The mixture was well stirred and dried (as described with reference to the flowcharts hereinabove). The dry product obtained had properties in the range of those described in Table 1 hereinabove.

Example 14
To 1000 ml of natural soy milk (Alpro N.V., Wevelgem, Belgium) 6.7 g of composition (prepared as described in Example 13) was added under stirring, employing a laboratory magnetic stirrer, to form enriched soy milk. The initial concentration of calcium in the enriched soy milk was tested and found 1332 mg/liter. After storing for 6 days at 4 Degrees Celsius, the concentration of calcium in the enriched soy milk was tested again and found 1343 mg/liter.

Example 15

To 1000 ml of milk based cocoa beverage (Machlevot Yutveta, Israel) 2 g of composition (prepared as described in Example 1) was added under stirring, employing a laboratory magnetic stirrer, to form Calcium enriched beverage. The initial concentration of calcium in the enriched beverage was tested and found 1402 mg/liter. After storing for 6 days at 4 Degrees Celsius, the concentration of calcium in the enriched beverage was tested again and found 1390 mg/liter.

It is appreciated that certain features of the invention, which are, for clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention, which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable sub-combination.

Although the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art.
CLAIMS:

1. A dry calcium rich composition comprising:
   (i) at least one source of calcium;
   (ii) at least one source of metal that is an alkaline metal other than calcium or a alkali metal; and
   (iii) at least one source of citrate;

wherein the composition has a bulk density of less than 0.4-0.5 g/cm³, comprises at least 15% (wt/wt) calcium and at least 66% (wt/wt) of citrate on dry weight basis.

2. A composition according to claim 1 comprising 15% to 20% (wt/wt) calcium and at least 71% (wt/wt) citrate on a dry basis.

3. A composition according to claim 1 wherein the calcium source is calcium hydroxide, calcium oxide, calcium carbonate, calcium propionate, calcium gluconate, calcium citrate, calcium stearate, calcium fumarate, or calcium glycerophosphate.

4. A composition according to claim 1 wherein the citrate source is citric acid, citric acid monohydrate, citric acid mono-, di- or tri-sodium salt, citric acid tripotassium salt or ammonium citrate.

5. A composition according to claim 1 wherein said source of metal is a source of sodium, a source of potassium, a source of magnesium or their mixtures.

6. A composition according to claim 5 wherein the potassium source potassium hydroxide, potassium citrate, potassium carbonate or potassium bicarbonate; the magnesium is selected from magnesium oxide, magnesium hydroxide, magnesium carbonate, or magnesium citrate; the sodium is selected from sodium hydroxide, sodium citrate, sodium carbonate or sodium bicarbonate.

7. A composition according to any one of claims 1 to 6 comprising a molar ratio of 3-4.5 citrate: 4-6 calcium: and 2-3 of at least one metal source.

8. A composition according to claim 7 comprising a molar ratio of citrate 3-4.5: calcium 4-6: potassium 2-3: and sodium or magnesium 0-1.

9. A composition according to claim 7 comprising a molar ratio of citrate 4: potassium 2: calcium 5.
10. A composition according to claim 1 further comprising stabilizers, coloring agents or emulsifiers.

11. A composition according to claim 1 in a dry form selected from powder, granules, flakes.

12. A composition according to claim 1 dissolved or suspended in an aqueous based solution.

13. A composition according to claim 1 further comprising at least one source of magnesium, wherein the composition has a bulk density of less than 0.5 g/cm³.

14. A composition according to claim 13, comprising a molar ratio of 3-4.5 citrate: 4-6 calcium: and 2-3 of the at least one metal source and magnesium.

15. A composition according to claim 14 comprising a molar ratio of citrate 3-4.5: calcium 4-6: potassium or sodium 2-3: and sodium and magnesium 0.1-1.

16. A composition according to claim 14 comprising a molar ratio of citrate 4: potassium 2: calcium 5.

17. A food or nutritional product comprising a composition according to any one of claims 1 to 16.

18. A product according to claim 17, being a beverage.

19. A beverage according to claim 18 wherein said beverage is a natural based beverage or a non-natural based beverage.

20. A beverage according to claim 19 wherein said natural based beverage is selected from fruit or vegetable based beverages or a milk based beverage.

21. A beverage according to claim 20 wherein said milk based beverage is soy milk, reconstituted milk formula, goat milk, sheep milk, camel milk, substitute milk, cow milk, oat milk, human milk or their mixtures.

22. A beverage according to any one of claims 18 to 21 further comprising flavorings, vitamins, minerals, proteins.

23. A beverage according to any one of claims 18 to 21, comprising at least 5gr/L to 8gr/L of the calcium rich composition.

24. A beverage according to any one of claims 18 to 23 being stable for a period of at least 70 days.

25. A method for producing a dried calcium-rich composition comprising:
(i) mixing at least one source of citrate with at least one source of calcium and at least one metal source selected from:
a) an alkaline earth metal source; and
b) an alkali metal source;
in a molar ratio of at least three moles citrate, at least five moles of calcium and at least two moles of the at least one metal source so as to produce an organic calcium solution; and
(ii) drying the organic calcium solution so as to produce the dried calcium-rich composition, wherein said composition comprises at least 66% citrate on a dry weight basis, and wherein said composition comprises at least 15% calcium on a dry weight basis.
1/2

104
Mix organic acid with calcium source
102
110
106
120
124
Add at least one metal source
126
130
Dry composition
138
136
100
FIG. 1

204
Mix citric acid in water
202
210
206
220
224
Add calcium source
226
200
FIG. 2

304
Mix citric acid in water
302
310
306
320
324
Add at least one metal source
306
326
330
334
Add calcium source
326
330
336
Dry composition
348
346
FIG. 3
FIG. 4

2/2

Mix dried composition with beverage/food

Store enriched beverage/food

Dilute enriched beverage/food

FIG. 5

Mix dried composition with water

Add wet composition to food/beverage

Store enriched wet food/beverage
Mix organic acid with calcium source

Add at least one metal source

Dry composition