



**Milk, milk-based beverage or dietetic product enriched
in calcium and process for its preparation**

The invention concerns the enrichment in calcium of a milk,
5 a milk-based beverage or a dietetic product.

Calcium is an important element in the nutrition of
mammals, in particular humans. Calcium is necessary for
the formation of bones and the maintenance of their quality
10 and is indispensable for metabolism.

Milk products, in particular milk, are an important source
of calcium. Unfortunately, many people do not consume the
quantity of milk necessary for their nutritional needs.
15 One litre of milk generally contains approximately 1250 mg
of calcium.

The enrichment in calcium of milk or of dietetic products
having a composition similar to that of milk encounters
20 technological problems when it is desired to manufacture
non-acid liquid products, in particular long life products,
for example ultra-pasteurized or sterilized products. In
point of fact, many potentially useful calcium salts are
soluble in water, so that the solution consisting of adding
25 these salts directly to the raw material and then
subjecting the mixture to heat treatment, in particular
ultra-pasteurization or sterilization, is not generally
possible, since this heat treatment leads to a finished
product which is degraded from the point of view of
30 physico-chemical stability and organoleptic properties.
The addition of insoluble salts before heat treatment does
not have the aforementioned disadvantages, but on the other
hand these salts settle rapidly at the bottom of the
package.

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A solution to this problem is provided, for example, by the
process according to EP-A-0 285 795. It consists of adding
thickening or gelling agents to a suspension of calcium
salt, of heat treating the mixture and then aseptically

metering it in a production line for a previously sterilized milk product.

5 The addition of calcium salts and polyphosphate to a whole milk before UHT treatment is known, for example, from AU-A-88768/82. In this patent application, the addition of a calcium salt in the presence of polyphosphate aims at stabilizing the milk by preventing it gelling with time during storage.

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The invention aims at providing a milk, a milk-based beverage or a dietetic product enriched in calcium, which is heat treated, neutral and homogeneous and free from thickening or gelling agent and which does not have the
15 aforementioned disadvantages.

Accordingly, the invention concerns a milk, a milk-based beverage or a dietetic product enriched in calcium, in liquid form and heat treated, characterized in that it
20 contains a quantity of calcium in a soluble form at least 20 % greater than that naturally contained in milk, which is free from a thickening or gelling additive, that its pH is close to the natural pH of milk and that it remains homogeneous without the well-known phase separation or
25 adverse changes to the taste and storage during its keeping period.

Within the context of the invention, milk is understood to be animal milk, from cows, sheep, goats or camels. It may
30 be a vegetable milk, for example soya. A beverage or dietetic product is understood to be a product which is nutritional in nature and has a composition similar to that of milk, intended for feeding children, adolescents or adults.

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A milk of this type, a beverage containing such a milk or a

dietetic product may be whole, semi-skimmed or skimmed, containing 0 to 3.6 % by weight of fats.

5 The source of calcium consists of a calcium salt, the solubility of which at a neutral or close to neutral pH ensures the absence of crystallization in the milk or the dietetic product after heat treatment, as well as the absence of reactivity under heat-treatment conditions. When it is not soluble enough, it precipitates forming a
10 deposit. If on the other hand its solubility is too high, there is a risk of reaction between the free calcium and proteins leading to coagulation during heat treatment.

The calcium salt fulfilling the aforementioned conditions
15 is preferably a salt of an organic acid selected from calcium glycerophosphate, gluconate and lactate, a calcium salt of an amino acid and mixtures thereof.

The enrichment in calcium corresponds to at least 20 %, and
20 preferably approximately 50 % compared with the quantity naturally contained in the milk.

The invention also concerns a process for enriching milk or a dietetic product in calcium, characterized in that the pH
25 of a liquid milk base is adjusted if necessary to a value of between 6.6 and 7.2, that a soluble calcium salt of an organic salt is added to it, and that the mixture is then subjected to UHT treatment and packaged.

30 A milk base may be a milk, preferably a semi-skimmed or skimmed milk, or a dietetic product with a composition similar to milk. Such a base may be a raw milk, a heat treated milk, a bactofugated milk or a pasteurized milk. It may have been reconstituted by recombination from skimmed
35 milk powder, anhydrous milk fats and water.

The calcium salt is preferably selected from calcium glycerophosphate, gluconate, and lactate and the calcium salts of amino acids and mixtures thereof.

5 According to the desired degree of enrichment, the solubility of the calcium salt and the UHT treatment conditions, the salt or the mixture in question will represent preferably 0.3 to 0.9 % by weight of the final milk product. For example, if the product is pasteurized,
10 the quantity added may be greater than in the case of a more stringent ultrapasteurization or sterilization.

If the gluconate is used, the preferred concentration is 0.6 to 0.9 % by weight. For a mixture of gluconate and
15 lactate, the preferred concentrations are 0.3 to 0.6 % by weight for gluconate and < 0.2 % by weight for lactate.

A preferred amino acid salt consists of a pidolate or a pyroglutamate, its preferred concentration being 0.4 to
20 0.6 % by weight.

According to a particularly preferred embodiment of the process, calcium glycerophosphate is added to the liquid product as a source of calcium in the presence of a calcium
25 chelating agent. The calcium chelating agent of choice consists of a citrate salt of an alkali metal, preferably trisodium citrate.

Calcium glycerophosphate constitutes a preferred source for
30 the enrichment in particular of a skimmed milk, in as much as it has the unexpected additional advantage of whitening the product, which overcomes the known disadvantage of the greenish coloration of low-fat milks which have been subjected to UHT treatment.

35 Use is preferably made of 0.3 to 0.5 % by weight of

glycerophosphate and 0 to 0.15 % by weight of chelating agent.

According to an alternative embodiment of the process,
5 suited in particular to the case of an enrichment at a high level with calcium salts which are likely to react with the milk proteins under the conditions of a relatively stringent UHT heat treatment, an aqueous suspension or solution is prepared of a calcium salt of an organic acid,
10 in particular selected from calcium glycerophosphate, gluconate, and lactate, and a calcium salt of an amino acid and mixtures thereof, its pH is adjusted to a value of between 6.6 and 7.2, the suspension or solution is heat treated and it is then metered aseptically in-line into the
15 previously sterilized or ultrapasteurized milk base.

The following examples illustrate the invention. In these, parts and percentages are by weight, unless indicated to the contrary.

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Example 1

397 kg of skimmed raw milk were subjected to pasteurization at 85°C for 10 s, and were then cooled to 40°C. 1.88 kg of
25 calcium glycerophosphate, the solubility of which in cold water is 2 %, and 0.58 kg of trisodium citrate were mixed with 20 kg of this raw material and the mixture was added to the remainder of the raw material. After adjusting the pH to 6.7 by adding 336 g of a 30 % aqueous suspension of
30 calcium hydroxide, the liquid was heated to 78°C and was then ultrapasteurized by UHT with direct steam injection at 138°C for 2 s. After cooling the liquid to 78°C by flash expansion, it was homogenized in two stages at 150 bar and then at 50 bar, cooled to 4°C and then packaged in brick
35 packages, all the operations following ultrapasteurization

taking place aseptically.

The calcium content was 2000 mg/l, which was the equivalent of an enrichment of approximately 65 % with respect to the milk.

After 45 days storage in a refrigerated circuit, no phase separation was observed nor any adverse changes to the taste. In addition, the milk had a pure white colour, unexpected for a low-fat milk, which corresponded approximately to that of a milk with 2 % fats.

Example 2

The procedure was as in example 1, except that 1.52 kg of glycerophosphate and 0.4 kg of trisodium citrate were used and the UHT treatment took place at 148°C for 5 s.

The properties of the product obtained were the same as in example 1. The calcium content was 1850 mg/l, which corresponded to an enrichment of approximately 50 % with respect to the milk.

Example 3

The procedure was as in example 1, using 0.35 % of calcium gluconate. The calcium gluconate was added to the previously pasteurized milk and the pH of the mixture was adjusted with a solution of NaOH and/or $\text{Ca}(\text{OH})_2$ and/or KOH to the natural pH of milk. The mixture was then ultra-pasteurized at 138°C for 2 s, cooled to 4°C and packaged aseptically.

Example 4

A skimmed raw milk was pasteurized at 85°C for 10 s and the

pH was then adjusted to 6.8 by adding an aqueous suspension of NaOH. The milk was reheated to 78°C and ultrapasteurized by UHT at 138°C for 2 s.

5 A 40 % aqueous suspension of calcium gluconate was prepared separately and its pH was adjusted to 6.7 by adding a 30 % aqueous suspension of NaOH and/or $\text{Ca}(\text{OH})_2$ and/or KOH. The suspension was heat treated and then metered in a hygienic manner into the previously ultrapasteurized milk, so that
10 the gluconate content corresponded to 0.65 % in the final product.

The mixture was cooled and packaged hygienically in brick packages.

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The product obtained contained 1800 mg of calcium per litre, which corresponded to an enrichment of 44 % with respect to the milk.

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Example 5

The milk base, which consisted of a milk with 1.5 % fats, was sterilized by UHT at 148°C for 5 s.

25 The procedure was as in example 4, with a source of calcium consisting of an aqueous solution of calcium lactate/ gluconate, the concentration of which corresponded to 38 % at 90°C, and the pH was adjusted to 6.7, it was heat treated and then metered aseptically into the sterilized milk base,
30 so that the lactate content was 0.2 % and that of the gluconate was 0.325 % in the final product.

The mixture was cooled to 4°C and then packaged hygienically in brick packages.

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The product obtained contained 1800 mg of calcium per litre, which corresponded to an enrichment of approximately 44 % with respect to the milk.

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Example 6

The procedure was as in example 4, with a source of calcium consisting of a 40 % aqueous suspension of pidolate (pyroglutamate) in a quantity corresponding to a concentration of 0.45 % in the final product, all other
10 conditions of the process being identical.

The product obtained contained 1800 mg of calcium per litre, which corresponded to an enrichment of approximately 44 % with respect to the milk.

Claims :

1. A UHT-treated milk product comprising a milk base containing constituents of calcium glycerophosphate in solution and constituents of a chelating agent in solution wherein based upon the milk product weight, the calcium glycerophosphate constituents are an amount, by dry weight, of from 0.3% to 0.9% and the chelating agent constituents are present and in an amount, by dry weight, of up to 0.15%.

2. A milk product according to claim 1 wherein the milk product does not contain an added thickening or gelling agent.

3. A milk product according to claim 1 wherein the calcium glycerophosphate constituents are in an amount of from 0.3% to 0.5%.

4. A milk product according to claim 1 wherein the chelating agent is selected from the group consisting of trisodium citrate and tripotassium citrate.

5. A milk product according to claim 1 wherein the milk base is a skimmed milk.

6. A process for obtaining a UHT-treated milk product enriched with calcium comprising adding calcium glycerophosphate and a calcium chelating agent to a milk base to obtain a calcium-enriched milk base having an amount of calcium at least 20% greater than a calcium amount contained by the milk base, adjusting the pH of the enriched milk base to a pH of between 6.6 to 7.2 to obtain a pH-adjusted product, subjecting the pH-adjusted product to UHT treatment to obtain a UHT-treated calcium-enriched milk product and packaging the enriched milk product.

7. A process according to claim 6 wherein no thickening or gelling agent is added to the milk base, to the enriched milk base or to the pH-adjusted product prior to the heat treatment so that the enriched milk product packaged is free of added thickening and gelling agents.

8. A process according to claim 6 wherein the calcium chelating agent is selected from the group consisting of trisodium citrate and tripotassium citrate.

9. A process according to claim 6 wherein, by weight based upon the enriched milk product weight, the calcium glycerophosphate is added to the milk base in an amount of from 0.3% to 0.9%.

10. A process according to claim 9 wherein the amount of calcium glycerophosphate is from 0.3% to 0.5% and the chelating agent is added in an amount so that the constituents of the chelating agent are present in the enriched milk product in an amount, by dry weight, of up to 0.15%.