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(54) Titre : CONFISERIE CONGELEE
(54) Title: FROZEN CONFECTION

(57) Abrégé/Abstract:
A frozen confection having a pH of from 2.7 to 4.7 is provided. The frozen confection comprises at most 1.0 wt% milk protein, 0.1 to 5.0 wt% of calcium sulphate and 0.1 to 5.0 wt% of citric acid or malic acid or a mixture thereof. A process for manufacturing the frozen confection is also provided.

Abstract

A frozen confection having a pH of from 2.7 to 4.7 is provided. The frozen confection comprises at most 1.0 wt% milk protein, 0.1 to 5.0 wt% of calcium sulphate and 0.1 to 5.0 wt% of citric acid or malic acid or a mixture thereof. A process for manufacturing the frozen confection is also provided.

Frozen Confection

Technical Field of the invention

The present invention relates to frozen confections such as water ices, fruit ices, sorbets and the like. In particular, the present invention relates to frozen confections which are "tooth-friendly".

Background to the invention

Water ices, fruit ices, sorbets and similar products are often designed for children. These products generally do not contain milk protein. They are typically fruit-flavoured and therefore contain acids such as citric acid or malic acid, and normally have a pH of about 4 or below. However, parents are reluctant to let their children consume such products since acids are known to be damaging to teeth. This is due to the demineralization of hydroxyapatite, a major constituent of tooth enamel. In low pH environments the hydroxyapatite molecules dissociate and calcium and phosphate ions are lost according to the following equation:

$$Ca_{10}(PO_4)_6(OH)_2 + 8H^+ \rightarrow 10Ca^{2+}(aq) + 6HPO_4^{2-}(aq) + 2H_2O$$

Simply raising the pH of the product is not satisfactory since although this reduces demineralization of tooth enamel, it creates another problem, namely that the frozen confection loses its characteristic acidic taste and palatability.

It has been proposed to add sources of calcium and / or phosphate ions to acidic foods and drinks in order to reduce tooth damage. For example, US 7 279 152 discloses acidic oral compositions, in particular beverages, which contain polyphosphate optionally in combination with a calcium salt in order to reduce tooth damage. Nonetheless, there remains a need for improved acidic frozen confections that are more "tooth-friendly".

Brief Description of the Invention

We have identified for the first time a further specific problem that exists when adding a source of calcium ions to frozen confections which contain citric and / or malic acid. Calcium salts of weak acids, such as lactic acid or phosphoric acid, react with the acid present in the frozen confection. For example, calcium lactate reacts with citric acid to form lactic acid and calcium citrate. This results in an undesirable taste caused by the

lactic acid and also reduced levels of calcium ions in the mouth because calcium citrate is poorly soluble. We have now found that damage to teeth caused by acidic frozen confections can be reduced whilst retaining the desired organoleptic properties of the frozen confection by selecting a particular calcium salt. Accordingly, in a first aspect, the invention provides a frozen confection having a pH of from 2.7 to 4.7 and comprising (by weight of the confection):

- at most 1.0 wt% milk protein;
- 0.1 to 5.0 wt% of calcium sulphate; and
- 0.1 to 5.0 wt% of citric acid or malic acid or a mixture thereof.

Frozen confections comprising calcium sulphate ($CaSO_4$) produce a high concentration of calcium ions in the mouth since calcium sulphate is highly soluble in water. In addition, calcium sulphate is the salt of a strong acid (sulphuric acid) and therefore does not react with citric / malic acid present in the frozen confection. Calcium sulphate has further advantages over other calcium salts which have been previously suggested for use in acidic food compositions. For example, calcium chloride is not suitable for frozen confections since it imparts a salty taste; nor is calcium nitrate since it results in food products which contain high nitrate levels. Calcium hydroxide, calcium carbonate and calcium hydrogen carbonate all react with organic acids which results in an increased pH which reduces the perception of acidic taste and can cause undesirable generation of gas.

Preferably, the frozen confection comprises from 0.01 to 1.0 wt% of a phosphate salt, more preferably from 0.02 to 0.1 wt%. Preferably the phosphate salt is a sodium phosphate, a potassium phosphate or a mixture thereof.

Preferably, the frozen confection has a pH of from 2.8 to 4.0.

Preferably, the frozen confection comprises from 0.15 to 1.0 wt% calcium sulphate.

Preferably, the frozen confection comprises citric acid or malic acid or a mixture thereof in an amount of from 0.15 to 3.0 wt%.

Preferably the frozen confection comprises at most 1.0 wt% fat.

Preferably, the frozen confection is a water ice, fruit ice or sorbet.

In a related aspect, the invention provides a process for manufacturing a frozen confection according to the first aspect of the invention, the process comprising the steps of:

(a) preparing a mix having a pH of from 2.7 to 4.7 and comprising at most 1.0 wt% milk protein, 0.1 to 5.0 wt% of calcium sulphate and 0.1 to 5.0 wt% of citric acid or malic acid or a mixture thereof;

(b) pasteurising and optionally homogenising the mix; then

(c) freezing and optionally aerating the mix to produce the frozen confection.

Detailed Description of the Invention

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. Definitions and descriptions of various terms and techniques used in frozen confectionery manufacture are found in Ice Cream, 6th Edition, R. T. Marshall, H. D. Goff and R. W. Hartel (2003), Kluwer Academic/Plenum Publishers. All percentages, unless otherwise stated, refer to the percentage by weight.

The frozen confection of the invention is preferably a water ice, a fruit ice or a sorbet. Water ice typically contains 15–25 wt% sugars / sweeteners / sugar replacers, together with stabilisers, colours and flavourings. Fruit ices are similar to water ices but also contain at least 10% fruit. Fruit means the edible part of fruit or the equivalent as juice, extracts, concentrated or dehydrated products and so on. Fruit, pulp, juice or any other preparation may be used either fresh or preserved. Sorbets are aerated products. In addition to the ingredients present in water ices and fruit ices, they typically contain a whipping or aerating agent. Proteins (e.g. milk protein) are generally not present in water ices, fruit ices and sorbets, except in small amounts as stabilisers (e.g. gelatin) or aerating agents (e.g. hydrolysed whey protein). Accordingly, the frozen confection comprises at most 1 wt%, more preferably at most 0.5 wt% and most preferably no milk protein. Fats are generally not present in water ices, fruit ices and sorbets. Accordingly, the frozen confection preferably comprises at most 1 wt%, more preferably at most 0.5 wt% and most preferably no fat.

The pH of the frozen confection means the pH when in liquid form, e.g. as an unfrozen mix or after melting, measured at room temperature (18°C). Water ices, fruit ices and sorbets typically have a low pH in order to provide favourable organoleptic properties such as acidic taste and palatability. If the pH is too high, the organoleptic perception of acidity is reduced. Accordingly the frozen confection has a pH of at most 4.7, preferably at most 4.0, more preferably at most 3.4. The frozen confection has a pH of at least 2.7, preferably at least 2.8, more preferably at least 3.0.

The frozen confection comprises up to 5 wt%, preferably up to 1 wt%, more preferably up to 0.4 wt% of calcium sulphate. The calcium sulphate is present in an amount of at least 0.1 wt%, preferably at least 0.15 wt% and more preferably at least 0.2 wt%.

The frozen confection comprises up to 5 wt%, preferably up to 3 wt%, more preferably up to 1 wt% of citric acid or malic acid or a mixture thereof. The citric acid or malic acid or a mixture thereof is present in an amount of at least 0.1 wt%, preferably at least 0.15 wt% and more preferably at least 0.2 wt%.

The frozen confection preferably comprises up to 1 wt%, more preferably up to 0.1 wt%, most preferably up to 0.05 wt% of a phosphate salt. The phosphate salt is preferably present in an amount of at least 0.01 wt%, more preferably at least 0.02 wt%, most preferably at least 0.03 wt%. Phosphate salts are defined as simple salts of phosphoric acid comprising one or more cations and one or two phosphate ions (PO_4^{3-}). Suitable phosphate salts include tri-sodium phosphate, di-sodium hydrogenphosphate, sodium dihydrogenphosphate, tri-potassium phosphate, di-potassium hydrogenphosphate, and potassium dihydrogenphosphate. Mixtures of the phosphate salts may be used. The phosphate salt is preferably highly soluble in water so that the frozen confection contains a high level of phosphate ions. In particular, the phosphate salts used in the invention are more soluble than polyphosphates comprising more than two phosphate ions. The polymer of phosphoric groups in polyphosphates is relatively stable in an aqueous solution and does not hydrolyse readily to provide high levels of phosphate ions.

Examples

Frozen confections were prepared using the formulations shown in Table 1. Examples 1 and 2 demonstrate frozen confections according to the invention. The comparative example is a conventional frozen confection.

Table 1 – Frozen confections

Ingredient (wt%)	Comparative example	Example 1	Example 2
Dextrose monohydrate	5.4	5.4	5.4
Sucrose	16.7	16.7	16.7
Locust bean gum	0.2	0.2	0.2
Citric acid	0.4	0.4	0.4
Lemon juice concentrate (40°Brix)	0.7	0.7	0.7
Flavour	0.3	0.3	0.3
Colour	0.01	0.01	0.01
Calcium sulphate ($CaSO_4$)	0	0.2	0.4
Sodium dihydrogen phosphate (NaH_2PO_4)	0	0.02	0.04
Water	to 100%	to 100%	to 100%
pH	3.1	3.1	3.1

Water ice products in the form of ice lollies (approximately 100mls in volume) on sticks were prepared as follows. First the dry ingredients were mixed with hot water and stirred until they had completely dissolved. The mixes were then pasteurized at 83°C for 20 seconds, cooled to room temperature (18°C) and the pH of each mix was measured. The mixes were poured into moulds immersed in a brine bath at -40°C and sticks were inserted when the mix was partially frozen. After the products had frozen, they were removed from the moulds and stored at -18°C.

Enamel blocks were cut from bovine incisors. Seven blocks were used for each example. They were hand-polished using 9 micron alumina so that the surfaces and edges were uniform. The Knoop hardness of each block was measured using a Mitutoyo MVK-H1 Vickers micro-hardness tester. 16 indents were made per block and the mean value was calculated. The blocks were then placed on mounting poles using ribbon wax; nail varnish was then painted around the edges of the blocks to limit the exposed surface

area to the enamel face only. Samples (2 ml) of the water ices of Examples 1 and 2 and the comparative example were cut, placed in 7ml containers and warmed up to 37°C. The enamel blocks were immersed in the melted water ices for 30 minutes. After the treatment the blocks were rinsed with copious amounts of deionised water, and the hardness was measured again. The decrease in hardness was calculated as the percentage difference between the initial hardness before immersion and the final hardness after immersion. The results are given in table 2.

Table 2 - Change in hardness of tooth enamel

	Initial hardness	Final hardness	% Decrease
Comparative example	198 ± 10	132 ± 14	33
Example 1	202 ± 4	169 ± 3	16
Example 2	202 ± 5	167 ± 5	17

Table 2 shows that there was a large decrease in the hardness of the enamel after exposure to the comparative example (33%) whereas examples 1 and 2 according to the invention resulted in much smaller decreases (16% and 17% respectively). This shows that frozen confections of the invention are more tooth-friendly than conventional frozen confections.

Examples 1 and 2 were tasted and were found to have organoleptic properties comparable to conventional frozen confections.

The various features of the embodiments of the present invention referred to in individual sections above apply, as appropriate, to other sections mutatis mutandis. Consequently features specified in one section may be combined with features specified in other sections as appropriate. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are apparent to those skilled in the relevant fields are intended to be within the scope of the following claims.

Claims

1. A frozen confection having a pH of from 2.7 to 4.7 and comprising:
   - at most 1.0 wt% milk protein;
   - 0.1.0 to 5.0 wt% of calcium sulphate; and
   - 0.1 to 5.0 wt% of citric acid or malic acid or a mixture thereof.

2. A frozen confection according to claim 1 which comprises from 0.01 to 1.0 wt% of a phosphate salt.

3. A frozen confection according to claim 2 wherein the phosphate salt is present in an amount of from 0.02 to 0.1 wt %.

4. A frozen confection according to claim 2 or claim 3 wherein the phosphate salt is a sodium phosphate, potassium phosphate or a mixture thereof

5. A frozen confection according to any of claims 1 to 4 wherein the pH is from 2.8 to 4.0.

6. A frozen confection according to any of claims 1 to 5 wherein the calcium sulphate is present in an amount of from 0.15 to 1.0 wt %.

7. A frozen confection according to any of claims 1 to 6 wherein the total amount of citric acid and malic acid is from 0.15 to 3 wt%.

8. A frozen confection according to any of claims 1 to 7 which comprises at most 1.0 wt% fat.

9. A frozen confection according to any of claims 1 to 8 which is a water ice, fruit ice or sorbet.

10. A process for manufacturing a frozen confection according to any of claims 1 to 9, the process comprising the steps of:

(a) preparing a mix having a pH of from 2.7 to 4.7 and comprising at most 1.0 wt% milk protein, 0.1 to 5.0 wt% of calcium sulphate and 0.1 to 5.0 wt% of citric acid or malic acid or a mixture thereof;

(b) pasteurising and optionally homogenising the mix; then

(c) freezing and optionally aerating the mix to produce the frozen confection.