

Food Process

5 The present invention relates to a process for
the production of a whey product which contains whey
proteins in a form which is heat stable at a neutral
pH.

A process is known for the production of a whey
protein product which is heat stable at a pH of ≤ 4.0
10 and has a weight ratio of calcium:protein of 0.2-5:100,
ash:protein of 2-20:100 and calcium:ash of 2-35:100.
This known product should have a protein content of
greater than 50% based on dry matter and is produced
from whey by firstly, adjusting the ratio of calcium:
15 protein to a value of 3-9:100 and subsequently carrying
out molecular separation at a pH value of 6.5 or 3.0.
This known product is intended for supplementing
carbonated or uncarbonated fruit-flavoured acidic
beverages. The acidic beverages which have been
20 supplemented in this manner may be sterilised by
heating without any protein precipitating.

However, there are other instances where whey
proteins are required to be heat stable but where the
above-mentioned known processes do not always attain
25 the desired result. This is notably the case for some

5 beverages which have a neutral pH and which are to a large extent composed of whey proteins and even more so for some types of milk which have been modified for the needs of infants.

Thus an object of the present invention is to provide a process for the production of a whey product which contains whey proteins in a form which is heat stable at a neutral pH value.

10 To this end, the process according to the present invention is characterised in that an aqueous solution is prepared which contains whey proteins in a form which has not been rendered insoluble and the Ca, Mg, citrate and/or phosphate concentrations in the solution (expressed in
15 mM) are adjusted, as is its pH value, to conform to the following numerical relationships:

$[Ca + Mg] - [citrate] \leq 0$ when $5.5 \leq pH \leq 6.2$

$[Ca + Mg] - [citrate] \leq 4$ when $6.2 \leq pH \leq 7.2$ and

$[Ca + Mg] - [citrate + phosphate] \leq 4$ when $7.2 \leq pH \leq 9.0$.

20 It was established that the calcium:protein ratio, as used in the above-mentioned prior art, could not be relied upon to prevent the heated whey proteins from precipitating at a neutral pH.

In this context, the terms Ca, Mg, citrate and
25 phosphate are to be understood as designating the free

form and the bound form of the ions concerned. Thus, by way of example, the symbol Ca is to be understood as designating not only the ionized form Ca^{++} but also the chelated form of calcium and it is the total calcium concentration which is to be included in the above-mentioned relationships.

Moreover, in this context, the proteins are regarded and determined as being total nitrogen multiplied by 6.38.

The term "neutral pH" is to be understood, in this context, as designating a pH of about pH 7, which does not fall below pH 5.5 or exceed 9.0 and is preferably within the narrower limits of, for example, pH 6.5 and pH 7.5. This latter range includes typical pH values of different types of milk which have been modified for the needs of infants.

Likewise, the term "proteins which are heat stable" is to be understood, in this context, as designating proteins of which more than 80% remain soluble after a heat treatment corresponding to sterilization. The terms precipitate and precipitation are to be understood as meaning coagulation or rendering insoluble. In contrast, the meaning of denaturation is restricted, in this context, to an alteration in the structure of whey proteins by any treatment with heat, acid or base.

(14)

During the course of a harsh treatment and particularly during sterilization, this denaturation may cause an aggregation reaction and precipitation.

5 Whey proteins have been found to precipitate at a neutral pH under the effect of a heat treatment corresponding to sterilization even if the ratio of calcium: protein has an apparently low value. A detailed study of the mechanisms involved in this precipitation brought
10 to light various facts which enabled the present process to be perfected in a straight-forward, reliable and exact manner.

 The heat stability of the proteins in the products which were obtained by the present process was determined
15 by a suitable test which is clearly distinguishable from the two known methods which are currently used in this field. The first of these known methods consists of determining the denaturation of whey proteins by acidifying the substance to a pH of 4.6, centrifuging it and
20 determining the nitrogen in the supernatant. It has now been found that an identical heat treatment which causes similar denaturations may in fact have very varied effects on the solubility of the product, depending on which product is used, the pH at which heat treatment
25 takes place and the concentration of free calcium during

this treatment.

The second of these known methods is based on measuring the volume of the precipitate. The hydration of the precipitate has been found to vary depending on the conditions under which precipitation occurs. For this reason, it was decided to determine the stability of the whey proteins under heating by separating the precipitated proteins at the pH at which the heat treatment takes place, determining the nitrogen in the supernatant and calculating the stability by comparison with the initial quantity of nitrogen before it was subjected to heating.

An appropriate straight-forward test was devised on this principle and consists of introducing 10 ml of solution into a beaker, rapidly (about 20 s) raising the temperature to 95°C by steam injection and maintaining the solution at this temperature for 5 mins by bubbling in steam. The beaker is then plunged into a bath of running water, the contents of the beaker are poured into a 50 ml graduated flask, the flask is filled up to the 50 ml mark with distilled water, the solution is centrifuged at 2,500 g for 10 mins, the nitrogen content of the supernatant is determined, this is divided by the nitrogen content of the original solution and multiplied

by one hundred. In other words, the ratio of "nitrogen in solution after sterilization at the pH under consideration": "nitrogen in solution before sterilization" is
5 determined and expressed as a percentage.

This test has been confirmed as producing a result which is generally definitive and a decisive increase in the effect is not produced by extending the bubbling time with steam or increasing the temperature. It has
10 been found to be satisfactory from a practical point of view to keep the solubility of the proteins above 80% under these test conditions.

Thus, the above-mentioned detailed study of the mechanisms involved in precipitation was carried out
15 on the basis of this test by varying the material, the pH value and the ionic medium. The present process which is the product of this study surprisingly overcomes the significant problems which are met in practice. The process does not only have the advantage of being
20 straight-forward and easy to master but also guarantees that the product has the desired heat stability, that is, more than 80% of the whey protein remains soluble when subjected to a heat treatment corresponding to sterilization. The reliability of the process is even more
25 surprising when one considers the harshness of the heat

treatment which is used.

Any whey starting material containing whey proteins in a form which has not been rendered insoluble may be used in the present process. This starting material may be cheese whey and in particular so-called sweet whey, such as the whey which is produced by coagulating the casein with rennet, or so-called acid whey such as the whey which is produced by acid coagulation of casein. Whey which has been demineralized by, for example, ion exchange or electrodialysis may also be used as the starting material, as may a whey protein concentrate which has been produced by, for example, ultrafiltration or dialysis. The starting substance may equally well be in the form of an aqueous solution, a concentrate or a powder, but it must fulfill the condition that its proteins have not been rendered insoluble particularly during concentration or drying.

Sweet whey is preferably used which has optionally been demineralised, in particular by ion exchange, or ultrafiltrated and/or diafiltrated and/or concentrated by evaporation or reverse osmosis.

Whey may be used as such after it has optionally been demineralised, ultrafiltrated and/or diafiltrated or a concentrate may be diluted or a powder dissolved to

produce the aqueous solution. Extremely variable ionic compositions are obtained for the different whey products depending on the starting material, the method which is
5 used and the operating conditions.

Various means may be used to adjust the concentrations to conform to the above-mentioned relationships depending on the type of product to be made stable. In particular, the solution may be diluted with demineralised water;
10 or citrate and/or phosphate in the form of an appropriate chemical compound which may be chosen from suitable salts of sodium or potassium, for example, may be added, thereby masking the calcium and magnesium; or the pH value may be increased, thereby encouraging the formation
15 of calcium or magnesium complexes with the polyvalent anions which are present; or undesirable ions may be exchanged for desirable ions on ion exchangers or by electrodialysis. The product may also be dialysed or ultrafiltrated and/or diafiltrated at an acid pH that is
20 at a pH below the range delimited above for a neutral pH and preferably at a pH of about 4.5.

The pH may be adjusted by any appropriate method used in the food industry which is compatible with the present process. The simplest method of doing this is
25 to lower or increase the pH with, for example,

hydrochloric acid, citric acid or phosphoric acid or sodium or potassium hydroxide or sodium carbonate respectively.

Regarding the relationships between the Ca, Mg, citrate and/or phosphate concentrations and the pH, the limit of the molar concentration not to be exceeded for the sum of Ca and Mg after deduction of citrate and/or phosphate, on the one hand, varies as a function of the pH value and the phosphate, on the other hand, has a virtually imperceptible effect below pH 7.2. Therefore, the concentrations of Ca, Mg and citrate, expressed in mM, should be such the numerical relationship $[Ca + Mg] - [citrate]$ has a value less than 0 at a pH value of 5.5 to less than 6.2, whereas it may rise to about 4 at a pH of 6.2 to less than 7.2. Above 7.2, the numerical relationship $[Ca + Mg] - [citrate + phosphate]$ should be less than 4.

In view of this, it is possible that other calcium or magnesium complexes, such as with phytate, serine-phosphate, pyrophosphate and polyphosphates or with EDTA could be used. Their effectiveness was thus examined at appropriate pH values, but it is preferable in the present process only to adjust the concentration with elements which are naturally present in large quantities in whey.

Thus, the whey product which is produced by the

present process contains whey proteins in a form which is heat stable, that is more than 80% stable under the effect of heat so that its use in the manufacture of beverages which have a neutral pH value, and in particular in the manufacture of different types of milk which have been modified for the needs of infants, is compatible with heat treatments corresponding to the sterilization which is used in the manufacture or use of beverages of this type.

The following Examples illustrate the process according to the present invention. Percentages are given in percent by weight, unless otherwise specified.

In the following Examples, the ions are determined by the following methods:

- phosphate by the formation of phosphomolybdate following sulfuric acid digestion or dry ashing.
- citrate by pyridine and acetic acid.
- calcium and magnesium by atomic absorption after dry ashing.

The sum of the concentrations of Ca and Mg after deduction of the concentration of citrate and, if necessary, the concentration of phosphate is expressed as in the above-mentioned relationships.

All concentrations and molar concentrations (expressed as mM).

All the sterilization operations were carried out

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by heating the material to 95°C for 5 mins,, in accordance with the above-mentioned test.

5 The heat stability of the whey proteins is given as the ratio of "nitrogen in solution after sterilization at the pH value under consideration": "nitrogen in the solution before sterilization" which is expressed as a percentage and determined in accordance with the above-mentioned test.

10 Finally, the difference from 100% dry matter in the compositions corresponds to the lactose content.

Comparative Examples

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a) Sweet whey is partially dialysed against de-ionised water. The resulting product has a pH value of 8.2, a dry matter content of 5.3% after evaporation with the following composition:

20	proteins	65.7 %
	Ca	1.1 %
	Mg	0.17%
	ash	4.6 %
	citrate	0.54%
25	phosphate	0.92%

This gives a weight ratio of calcium:protein of 17:100, of ash:protein of 7:100 and calcium:ash of 24:100.

However, $[Ca + Mg] - [citrate] = 17.0$ and $[Ca + Mg] - [citrate + phosphate] = 11.9$.

Although this product has a composition corresponding to the definition given by the above-mentioned prior art, its proteins have a heat stability of less than 40% for a pH ranging from 4.5 to 8.0.

b) Sweet whey is ultrafiltrated in an industrial apparatus. The resulting product has a pH of 6.8, a dry matter content of 13.2% with the following composition:

	proteins	82.6 %
15	Ca	0.86%
	Mg	0.07%
	ash	2.8 %
	citrate	0.10%
	phosphate	0.95%

20 $[Ca + Mg] - [citrate] = 31.7$ and $[Ca + Mg] - [citrate + phosphate] = 18.4$.

Although this product also has a composition corresponding to the definition given by the above-mentioned prior art, its proteins have a heat stability of less than 25 60% at a pH value of 8.0 and even less at a pH value of 7.5.

Example 1

Sweet whey is produced from skimmed milk by adding rennet and heating to 40°C. to form the curds, but without pasteurising the milk. The whey is concentrated by evaporation under vacuum and is freeze-dried to produce a powder.

The powder is dissolved in demineralised water to reconstitute a solution which has the same composition as the original sweet whey. The pH of the solution is 6.0, the dry matter content is 6.0% which has the following composition:

proteins	12 %
Ca	0.46%
Mg	0.10%
ash	7.6 %
citrate	2.23%
phosphate	1.71%

$$[\text{Ca} + \text{Mg}] - [\text{citrate}] = 2.0$$

The value of $[\text{Ca} + \text{Mg}] - [\text{citrate}]$ is adjusted to - 3 by adding 5 mM of sodium citrate and the product is then sterilized. The proteins have a heat stability of 86%.

If, by way of comparison, an attempt is made to sterilize the solution as such, the heat stability of

the proteins is found to be less than 50%.

Example 2

5 Sweet whey which has been demineralised by ion exchange has a pH of 6.8 and a dry matter content of 6.0% which has the following composition:

	proteins	12.6 %
	Ca	0.02%
10	Mg	0.06%
	citrate	0.6%
	phosphate	0.3 %
	ash	0.52%

$$[Ca + Mg] - [citrate] = -0.1$$

15 Citric acid and calcium hydroxide are added in equi-molar quantities to adjust the calcium content of the product to 0.35% of dry matter. The pH is adjusted to 6.0 by adding NaOH. The product may be subsequently concentrated by evaporation and spray-dried or sterilized.
20 ized. The proteins of the product have a heat stability of 85%.

In contrast, if, by way of comparison, citrate and calcium are used in a molar ratio of 2:3 to adjust the calcium content of the product, the proteins have a
25 heat stability of less than 50%. In other words, more

than half the quantity of protein is rendered insoluble during evaporation and drying or sterilization. A further two mM of citrate are required to re-establish an ionic medium which ensures that the proteins have a heat stability of greater than 80%.

Example 3

Sweet whey is produced which has been demineralised to 85% by ion exchange or dialysis and has a pH of 6.7 and a dry matter content of 6.0 which has the following composition:

proteins	12 %
Ca	0.34%
Mg	0.03%
ash	2.0 %
citrate	0.4 %
phosphate	0.5 %

$[Ca + Mg] - [citrate] = 4.6$ and $[Ca + Mg] - [citrate + phosphate] = 1.4$

The pH of the product is adjusted to 7.5 by adding KOH and it may be sterilized. The heat stability of the proteins is greater than 80%.

In contrast, if, by way of comparison, the product is sterilized at a pH of from 6.5 to 7.0, too large a

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quantity of proteins precipitates. The heat stability of the proteins is less than 70%.

5 Example 4

4 mM of sodium or potassium citrate are added to demineralised whey of the type described in Example 3. The product may be sterilized at a pH value of from 6.5 to 7.0. The heat stability of the proteins is greater
10 than 80%.

Example 5

Demineralised whey of the type described in Example 3 is concentrated to 24% of dry matter. 18 mM of sodium
15 citrate is added and the concentrated whey may be sterilized. The heat stability of the proteins is greater than 80%.

Example 6

20 Demineralised whey of the type described in Example 3 is diluted in a proportion of 1 part by volume of whey for every 2 parts by volume of de-ionised or softened water and the diluted whey may then be sterilized. The heat stability of the proteins is greater than 80%.

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Example 7

A sweet whey concentrate is produced by ultrafiltration which has a pH value of 8.3 and a dry matter content of 8.4% with the following composition:

5	proteins	78 %
	Ca	0.88%
	Mg	0.08%
	ash	3.0 %
10	citrate	0.67%
	phosphate	1.0 %

The concentrate is diluted with demineralised water in a proportion of 1 part by volume of concentrate for every 4 parts of water and may then be sterilized. The heat stability of the proteins is 95%.

In contrast if, by way of comparison, the concentrate is not diluted it cannot be sterilized. The heat stability of the proteins is only 37%. If the concentrate is only diluted in a proportion of 1 part by volume of concentrate for 1 part of water, the heat stability of the proteins is still only 42%.

Examples 8 - 13

A sweet whey concentrate is prepared by ultrafiltration which has a pH value of 6.8 and a dry matter

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content of 13% with the following composition:

	proteins	82.6 %
	Ca	0.86%
5	Mg	0.07%
	ash	2.08%
	citrate	10.1 %
	phosphate	0.95%

[Ca + Mg]-[citrate] = 31.0 and [Ca + Mg]-[citrate +
10 phosphate] = 18.0

If, by way of comparison, the product is sterilized as such after the pH has been adjusted to any value ranging from 4.5 to 9.0, the heat stability of the proteins is always found to be less than 40%.

15 A whey product, of which the proteins have a heat stability of greater than 80%, is prepared from the same whey concentrate for each of Examples 8 to 13 according to various embodiments of the present process. The various embodiments are described in the following with reference to
20 the number of each Example. The numerical relationship of the composition based on dry matter: [Ca + Mg]-[citrate] when the pH value is < 7.2 and [Ca + Mg] - [citrate + phosphate] when the pH value is ≥ 7.2 , and the heat stability of the proteins of each of the products .
25 obtained are shown in the following table.

8. 15 mM of mono- or disodium phosphate are added to the product and the pH is adjusted to a value in the range from 7.2 to 9.0.
- 5 9. 15 mM of sodium citrate are added to the product and the pH is adjusted to a value ranging from 7.2 to 9.0.
- 10 10. The product is acidified to a pH of 5.0, dialysed against de-ionised water and the pH adjusted to a value ranging from 7.2 to 9.0.
11. The product is acidified to a pH of 4.5, dialysed against de-ionised water and the pH adjusted to a value ranging from 6.4 to 6.8.
- 15 12. The product is softened on a strong cationic ion exchanger (sulfoethyl cellulose) which has been regenerated with NaCl and the pH is adjusted to a value ranging from 6.0 to 7.0.
- 20 13. The product is demineralised on a strong cationic ion exchanger which has been regenerated by HCl and then on a strong anionic ion exchanger (diethylaminoethyl cellulose) which has been regenerated by NaOH and the pH is adjusted to a value ranging from 6.0 to 7.0.



	Original concentrate	Product according to Example No					
		8	9	10	11	12	13
Composition %							
protein	82.6	81.7	80.2	85.0	87.3	85.5	87.2
Ca	0.86	0.85	0.84	0.32	0.13	0.04	0.01
Mg	0.07	0.07	0.07	0.03	0.01	0.01	0.00
ash	2.8	3.82	3.5	1.7	0.7	2.4	0.4
citrate	0.1	0.1	2.2	0.04	0.14	0.04	0.02
phosphate	0.95	1.65	0.92	0.73	0.67	0.50	0.13
[Ca + Mg]- [citrate]	31.0				3.8	1.6	0.2
[Ca + Mg]- [citrate + phosphate]	18.0	3.0	3.0	1.5			
Stability under the effects of heat %	40	87	82	82	96	98	98.

In Example 9, the product is heated by steam injection to 140°C over a period of 10 mins. and the heat stability of the proteins remains above 95%.

Important Note

In this specification only an upper limit which must not be exceeded for the numerical relationship $[Ca+Mg]-[citrate]$ or $[Ca+Mg]-[citrate+phosphate]$ is considered.

5 The above-mentioned relationships between the Ca, Mg, citrate and/or phosphate concentrations and the pH are formulated accordingly. There is generally no question of a recommended lower limit. Indeed, the lower limit

10 will always be determined from a nutritional point of view and in particular in terms of the maximum citrate content of the product for the production of which the product obtained by the present process is used.

Therefore, in the above-mentioned relationships $[Ca+Mg]-[citrate]$ and $[Ca+Mg]-[citrate + phosphate]$ should

15 generally never be below -20.



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Claims

1. A process for the production of a whey product which contains whey proteins in a form which is heat stable at a neutral pH, which comprises preparing an aqueous solution containing whey proteins in a form which has not been rendered insoluble and adjusting the Ca, Mg, citrate and/or phosphate concentrations in the solution (expressed in mM) and the pH to conform to the numerical relationships:
- [Ca + Mg]-[citrate] is < 0 when $5.5 \leq \text{pH} < 6.2$
[Ca + Mg]-[citrate] is < 4 when $6.2 \leq \text{pH} < 7.2$ and
[Ca + Mg]-[citrate + phosphate] is < 4 mM when $7.2 \leq \text{pH} \leq 9.0$
2. A process according to Claim 1 wherein the aqueous solution is prepared with sweet or acid whey.
3. A process according to Claim 1 wherein the aqueous solution is prepared with sweet or acid whey which has been demineralised by ion exchange.
4. A process according to Claim 1, wherein the aqueous solution is prepared with sweet or acid whey which has been dialysed or ultrafiltrated and/or diafiltrated.



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5. A process according to any of Claims 1 to 4 wherein the above-mentioned concentrations are adjusted by diluting the solution with demineralised water.

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6. A process according to any of Claims 1 to 5 wherein the above-mentioned concentrations are adjusted by adding citrate and/or phosphate.

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7. A process according to Claim 4 wherein the above-mentioned concentrations are adjusted by dialysing or ultrafiltrating and/or diafiltrating sweet whey at an acid pH value and subsequently adjusting the pH value.

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