(19) **DANMARK**

(10) **DK/EP 2989897 T3**

Patent- og Varemærkestyrelsen

(12) # Oversættelse af europæisk patentskrift

(51) Int.Cl.:	*A 23 C 7/04 (2006.01)*	*A 23 C 1/14 (2006.01)*	*A 23 C 9/142 (2006.01)*
	A 23 C 9/146 (2006.01)	*A 23 C 19/00 (2006.01)*	*A 23 C 19/05 (2006.01)*
	B 01 D 61/02 (2006.01)	*B 01 D 61/14 (2006.01)*	*B 01 D 63/08 (2006.01)*
	B 01 D 63/10 (2006.01)	*B 01 D 71/06 (2006.01)*	*B 01 D 71/68 (2006.01)*

(45) Oversættelsen bekendtgjort den: **2018-05-07**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2018-02-21**

(86) Europæisk ansøgning nr.: **14182971.3**

(86) Europæisk indleveringsdag: **2014-08-30**

(87) Den europæiske ansøgnings publiceringsdag: **2016-03-02**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

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(54) Benævnelse: **Fremgangsmåde til fremstilling af farveløs ostemælk**

(56) Fremdragne publikationer:

EP-A2- 0 249 368
WO-A2-99/15023
US-A- 3 907 777
DATABASE WPI Week 198009 Thomson Scientific, London, GB; AN 1980-15915C XP002731623, & NL 7 808 199 A (NED INST ZUIVELONDE) 6. Februar 1980 (1980-02-06)

Description

FIELD OF THE INVENTION

The invention is in the field of dairy products and relates to a process for the production of colourless vat milk as a starting material for the production of colourless cheese.

PRIOR ART

Milk products are considered in Europe, North America and Australia to be basic foodstuffs. Cheese in this case is particularly widespread in Western culture. It is assumed that up to 5,000 cheeses are produced, although cheeses of the same denomination also differ from cheese dairy to cheese dairy. The country with the greatest cheese production worldwide is the USA. In East Asia, Africa and South America, cheese plays a minor role. One reason for this is the widespread lactose intolerance among the population.

Depending on the cheese type, between 4 and 16 litres of milk are required to produce one kilogram of cheese. On the basis of the production process, four types may be differentiated:

- sour milk cheese,
- fresh milk cheese or rennet cheese,
- whey protein cheese and
- whey cheese.

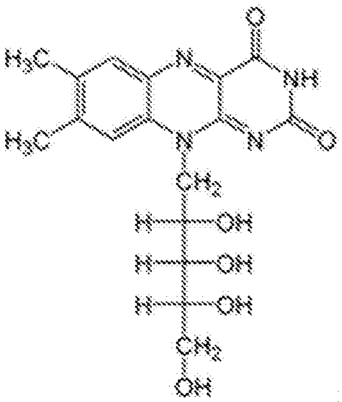
In the case of conventional cheese, the milk is first heated to 75 degrees and freed from spores in the bacterofuge. In the next step, the vat milk or cheese milk obtained in this manner is coagulated. This is achieved by adding lactic acid bacteria (for cream cheese and sour milk cheese) and/or rennet (for hard cheese, semi-hard cheese and soft cheese); here, calcium chloride and pigments are also added. If the milk is solid, the mass is divided into small pieces with a cheese harp: what is termed the cheese curd is formed. The smaller the parts become, the better the liquid whey drains off, and the harder the cheese becomes later. If the curd has achieved an appropriate consistency, it is skimmed off and shaped.

The cheese then has to ripen for different periods of time depending on the variety in order to develop its typical aroma and appearance. During its ripening period, the cheese wheels are regularly turned and brushed with salt. The salt removes moisture from the cheese, so that a solid rind is formed. At the same time, salt preserves the cheese and contributes to its taste.

Sour milk cheese is formed when milk is acidified by lactic acid bacteria and the milk protein (casein) is thereby precipitated. This process is termed coagulation. The precipitated casein is separated from the liquid, the whey, and is what is termed cream cheese. This can be used to produce ripened sour milk cheese, which can be refined by special bacteria cultures (red smear) or blue vein mould.

In the production of rennet cheese (also termed fresh milk cheese) the milk protein casein is precipitated by an enzyme mixture of pepsin and chymosin. The property of rennet which cleaves the milk protein casein in such a manner that the milk thickens without becoming sour, was already known in antiquity and utilised for cheese production. Most of the known hard or semi-hard cheese types originate from curdling of fresh milk. Cream cheese, although typically produced by curdling cultured milk with the aid of lactic acid bacteria, can be produced using rennet.

Raw milk which has been treated in the manner described above to form vat milk or cheese milk, however, has a high content of riboflavin (I).



(I)

Riboflavin, which also occurs in vegetables such as broccoli, rye, asparagus or spinach, and furthermore in fish, muscle meat, eggs and whole grain products, is also known as lactoflavin or vitamin B2. It is a derivative of pteridine, more precisely of isoalloxazine and the sugar alcohol ribitol. Riboflavin serves as a precursor of flavin coenzymes (FAD, FMN) which play a major role in particular in oxidoreductases, e.g. NADH-dehydrogenase. As a result, it plays a central role in metabolism. Because of its yellow colour, riboflavin is also used as a food dye (E101).

Although riboflavin is therefore in principle an interesting natural substance having a multitude of applications, it is undesirable as a milk constituent, since it gives the milk a distinct yellow tinge which deepens further during production of cheese from this milk. Even though this colouration is of no importance for the cheese aroma and wholesomeness, many consumers prefer cheese that is virtually colourless and at most has a very slight yellow colouring.

WO 99/15023 A2 discloses an adsorption process for separating a substance (e.g. riboflavin) from a solution (e.g. whole milk, skimmed milk, cream, whey, whey permeate or colostrum). The solution is treated with a resin that comprises particles with magnetic properties (e.g. magnesium silicate), whereby the substance to be separated binds to the resin. Finally, the substance to be separated is released using a suitable desorption agent.

EP 0 249 368 A2 relates to a process for obtaining lactose crystals from lactose-rich liquids, such as whey, milk or skimmed milk, although whey is preferred. Pasteurised whey is subjected to ultrafiltration according to the described process. The permeate obtained is then subjected to reverse osmosis. The reverse osmosis permeate is then subjected to clarification by centrifugation, and the permeate obtained is demineralised using electrodialysis or an ion exchanger. Riboflavin is then removed from the de-mineralised permeate by an adsorption process on activated carbon. After an additional filtration step, a syrup is obtained from which lactose can be crystallised.

NL 7 808 199 A discloses the reverse osmosis of an ultrafiltration permeate (from milk or whey). Neither the separation nor the recovery of riboflavin is disclosed in this document.

US 3 907 777 A relates to a process for removing riboflavin from whey. The process disclosed is characterised in that whey having a total solid content of 6.2-25% is passed through a column filled with granular activated carbon at a temperature of below 70°C to room temperature, in order to adsorb the riboflavin in the whey on the granular activated carbon, and the granular riboflavin-saturated activated carbon is regenerated for reuse by alternately passing through an aqueous sodium hydroxide solution and water.

Previous processes for separating off riboflavin have proved either to be too complex or too inefficient. Instead, in order to produce colourless cheese, white pigments, especially titanium dioxide are added to the vat milk, which is in itself undesirable in view of the fact that cheese is a natural product.

The object of the present invention is therefore to pre-treat vat milk in a simple manner and to remove the chromophore riboflavin therefrom so that the vat milk can be used directly for the production of colourless, i.e. non-yellow, cheese. In particular, the co-utilisation of white pigments should become superfluous. A second object of the invention is to isolate the valuable riboflavin from the milk in order to then be able to use it further for industrial purposes.

DESCRIPTION OF THE INVENTION

The present invention relates to a process for the production of colourless vat milk in which

(a) vat milk is subjected to an ultrafiltration and in the course of this a first permeate P1 and a first retentate R1 are produced, wherein the ultrafiltration is carried out using membranes that have a pore diameter from 5,000 to 50,000 Dalton,

(b) the permeate P1 is subjected to a reverse osmosis and in the course of this a second permeate P2 and a second retentate R2 are produced, wherein the reverse osmosis is carried out using semi-permeable membranes that have a selectivity from 10 to 1,000 Dalton,

(c) the second retentate R2 is treated with an adsorbent and in the course of this a further retentate R2* is produced,

(d) the resultant retentate R2* is combined with the retentate R1 and the permeate P2.

Surprisingly, it has been found that by a combination of ultrafiltration, reverse osmosis and adsorption process, the chromophore riboflavin can be virtually completely removed from the vat milk, such that a starting material is obtained in a simple manner which can be used without further measures, in particular without the addition of pigments, for the production of colourless cheese. The valuable riboflavin can, however, be isolated in high purity by simple desorption.

VAT MILK

The term vat milk or cheese milk denotes a raw milk which, after pasteurization and fat adjustment, is to be coagulated for the production of cheese, but also yoghurt. Since cheese production was previously predominantly carried out in vats—which is in part still typical for the production of parmesan today —vat milk is a term used synonymously.

In order that raw milk can be used for the production of cheese, it must conform to legal requirements which are laid down in the German regulations on cheese. Usually, the processing process begins with heating the raw milk by heat exchange with heat carrier media, and with simultaneous partial heat recovery. Separation into skimmed milk, cream and separator sludge is usually carried out in a pasteurisation unit with an integrated separator. In this case the heating is carried until a first thermisation or pasteurisation takes place. After it is subsequently standardised, the standardised milk is pre-stacked in a tank and the pre-stacked milk that is removed from the tank is usually subjected to a second pasteurization by repeated heating and then passed via a bacterofuge in order to reduce the bacterial count to the extent that is necessary for production and legal requirements.

The heat treatment of the raw milk (“sterilisation”) is preferably carried out in heat exchangers; plate heat exchangers have proved to be particularly suitable. On the heat exchangers there is a temperature gradient which, however, is selected such that the raw milk is heated to a temperature of approximately 70 to 80°C, and in particular approximately 72 to 74°C, for a residence time of at least 20 and at most 60 seconds, preferably approximately 30 seconds.

The separation of solids ("cheese dust") and the skimming of the fat content of approximately 4% by weight is usually carried out in a downstream component, preferably a separator. Such components are sufficiently known from the prior art. Very widespread in the milk industry are separators from GEA Westfalia Separator GmbH, with which the two steps can be carried out individually or together (http://www.westfalia-separator.com/de/anwendungen/molkereitechnik/milch-molke.html). Corresponding components are also described, for example, in **DE 10036085 C1** (Westfalia) and are very well known to the skilled person, so that no explanations are required to carry out these process steps, since they are considered part of general specialist knowledge.

ULTRAFILTRATION

The term ultrafiltration is understood to mean filtration through membranes having a pore size < 0.1 µm, whereas a filtration with pore sizes > 0.1 µm is usually referred to as microfiltration. Both cases are purely physical, i.e. mechanical, membrane separation processes which operate according to the principle of mechanical size exclusion: all particles in the fluids which are larger than the membrane pores are retained by the membrane. The driving force in both separation processes is the differential pressure between the inlet and outlet of the filter surface, which is between 10 kPa and 1,000 kPa (0.1 and 10 bar). The filter surface material can, depending on the field of use, consist of stainless steel, plastic, ceramics or textile fabric. There are various forms of the filter elements: candle filters, flat membranes, spiral wound membranes, pocket filters and hollow fibre modules, all of which are generally suitable for the purposes of the present invention.

Ultrafiltration is preferably carried out at temperatures in the range of 10 to 55, preferably 12 to 20°C, the membranes preferably having a pore diameter in the range of 5,000 to 50,000, and preferably 5,000 to 25,000 Dalton. Preferably, they are what is termed spiral wound membranes or plate-frame modules made of polysulfone or polyethylene membranes.

REVERSE OSMOSIS

Reverse osmosis is a process in which the feed material is dewatered using a semi-permeable membrane, as a result of which the concentration of valuable milk proteins is increased. The principle is to expose the system to a pressure which is higher than the pressure which results from the osmotic demand for concentration equilibration. As a result, the molecules of the solvent migrate against their "natural" osmotic propagation direction. The process forces them into the compartment in which the dissolved substances are present in less concentrated form. Milk has an osmotic pressure of less than 200 kPa (2 bar), the pressure employed for the reverse osmosis of milk is 300 kPa to 3000 kPa (3 to

30 bar), depending on the membrane and system configuration used. The osmotic membrane which permits only the carrier liquid (solvent) to pass through and retains the dissolved substances (solute) must withstand these high pressures. If the pressure difference more than compensates for the osmotic gradient, the solvent molecules pass through the membrane, as with a filter, whereas the milk proteins are retained. In contrast to a classical membrane filter, osmosis membranes do not have continuous pores. Reverse osmosis is preferably carried out at a temperature in the range from 10 to 55, preferably 10 to 20°C., with semi-permeable membranes that have a selectivity from 10 to 1,000 Dalton.

ADSORPTION

The riboflavin dissolved in the retentate R2 can be adsorbed in a manner known per se, for example by passing the retentate over a fixed bed containing an adsorbent or using a column equipped with an adsorbent for solid-liquid adsorption. Typical ion-exchange resins such as Lewatit resins are suitable adsorbents, but adsorption on activated carbon is preferred. Usually, the adsorption is carried out at temperatures in the range of 10 to 55°C, and in particular 12 to 20°C.

The adsorption of the riboflavin is virtually quantitative with a suitable amount of adsorbent and/or sufficient distance. Although amounts and distances may be easily determined by skilled persons themselves without having to be inventive, a preferred embodiment consists in filling a column having a diameter of approximately 10 cm and a length of approximately 100 cm with activated carbon (particle size e.g. D50 = 1 mm) and feeding the retentate R2 over it at a flow rate of 10 to 25 l/h.

RIBOFLAVIN ISOLATION

The invention further relates to a process for obtaining riboflavin in which

(a) vat milk is subjected to an ultrafiltration and in the course of this a first permeate P1 and a first retentate R1 are produced, wherein the ultrafiltration is carried out using membranes that have a pore diameter from 5,000 to 50,000 Dalton,

(b) the permeate P1 is subjected to a reverse osmosis and in the course of this a second permeate P2 and a second retentate R2 are produced, wherein the reverse osmosis is carried out using semi-permeable membranes that have a selectivity from 10 to 1,000 Dalton,

(c) the second riboflavin-containing retentate R2 is treated with an adsorbent and in the course of this a further retentate R2* is produced, wherein the adsorbent used is activated carbon, and

(d) the adsorbent is treated with a suitable desorbent, the amount of riboflavin dissolved therein is desorbed and is isolated by separating off the desorbent.

The adsorbent is, as already explained above, preferably activated carbon. For the desorption, preferably polar solvents are suitable, such as ethanol or isopropyl alcohol, which can then be removed again gently, for example on a rotary evaporator, in such a manner that the riboflavin is obtained virtually quantitatively as a yellow to orange residue.

The process is summarized again in the flowchart as per **Figure 1.**

EXAMPLES

EXAMPLE 1

100 l of raw milk were heated to 75°C for 10 seconds in a plate heat exchanger, pasteurized, and then sterilised in a bacterofuge. The resultant vat milk was then subjected to an ultrafiltration at 18°C using a sulfone spiral wound membrane having a pore diameter of 20,000 Dalton. The retentate R1 was pumped into an intermediate tank and the permeate P1 was subjected at 20°C to a reverse osmosis using a semi-permeable membrane having a selectivity of 500 Dalton. The permeate P2 was in turn pumped into an intermediate tank, whereas the retentate R2 was fed at 20°C over a column (diameter 10 cm, length 100 cm) filled with activated carbon, wherein the flow rate was approximately 20 l/h. The previously yellow-coloured left the column virtually colourless (retentate R2*), was combined with the retentate R1 and with the permeate P2 from the two intermediate tanks and was then available for the production of colourless cheese.

EXAMPLE 2

After the entire retentate R2 has passed through, the adsorption column, at this stage loaded with riboflavin, was rinsed at 20°C first in 3 portions each time with 10 l of ethanol each and then finally with 10 l of isopropyl alcohol. The four yellow-orange fractions were combined and then freed from the solvent in a vacuum. This resulted in 44 g of riboflavin remaining as a bright orange solid.

Patentkrav

1. Fremgangsmåde til fremstillingen af farveløs ostemælk, i hvilken

(a) ostemælk udsættes for en ultrafiltrering og hvorved et første permeat P1 og et første retentat R1 fremstilles, hvor ultrafiltreringen udføres under anvendelse af membraner, der har en porediameter fra 5,000 til 50,000 Dalton,

(b) permeatet P1 udsættes for en omvendt osmose og hvorved et andet permeat P2 og et andet retentat R2 fremstilles, hvor den omvendte osmose udføres under anvendelse af semipermeable membraner, der har en selektivitet fra 10 til 1,000 Dalton,

(c) det andet retentat R2 behandles med et adsorptionsmiddel og hvorved et yderligere retentat R2* fremstilles,

(d) det således opnåede retentat R2* kombineres med retentatet R1 og permeatet P2.

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** ultrafiltreringen (trin a) udføres ved en temperatur i området fra 10 til 55 °C.

3. Fremgangsmåde ifølge krav 2, **kendetegnet ved, at** ultrafiltreringen (trin a) udføres ved en temperatur i området fra 12 til 20 °C.

4. Fremgangsmåde ifølge mindst ét af kravene 1 til 3, **kendetegnet ved, at** ultrafiltreringen (trin a) udføres under anvendelse af spiralviklede membraner eller plade-ramme-moduler lavet af polysulfon eller polyethylenmembraner.

5. Fremgangsmåde ifølge mindst ét af kravene 1 til 4, **kendetegnet ved, at** den omvendte osmose (trin b) udføres ved en temperatur i området fra 10 til 55 °C.

6. Fremgangsmåde ifølge mindst ét af kravene 1 til 5, **kendetegnet ved, at** det anvendte adsorptionsmiddel er aktivt kul.

7. Fremgangsmåde ifølge mindst ét af kravene 1 til 6, **kendetegnet ved, at** det anvendte adsorptionsmiddel er et ionbytterresin.

8. Fremgangsmåde ifølge mindst ét af kravene 1 til 7, **kendetegnet ved, at** adsorptionen udføres ved temperaturer i området fra 10 til 55 °C.

9. Fremgangsmåde til udvinding af riboflavin, i hvilken

(a) ostemælk udsættes for en ultrafiltrering og hvorved et første permeat P1 og et første retentat R1 fremstilles, hvor ultrafiltreringen udføres under anvendelse af membraner der har en porediameter fra 5,000 til 50,000 Dalton,

(b) permeatet P1 udsættes for en omvendt osmose og hvorved et andet permeat P2 og et andet retentat R2 fremstilles, hvor den omvendte osmose udføres under anvendelse af semipermeable membraner der har en selektivitet fra 10 til 1,000 Dalton,

(c) det andet riboflavin-indeholdende retentat R2 behandles med et adsorptionsmiddel og hvorved et yderligere retentat R2* fremstilles, hvor det anvendte adsorptionsmiddel er aktivt kul, og

(d) adsorptionsmidlet behandles med et egnet desorptionsmiddel, hvor mængden af riboflavin opløst deri desorberes og isoleres ved at skille desorptionsmidlet fra.

10. Fremgangsmåde ifølge krav 9, **kendetegnet ved, at** det anvendte desorptionsmiddel er ethanol eller isopropylalkohol.

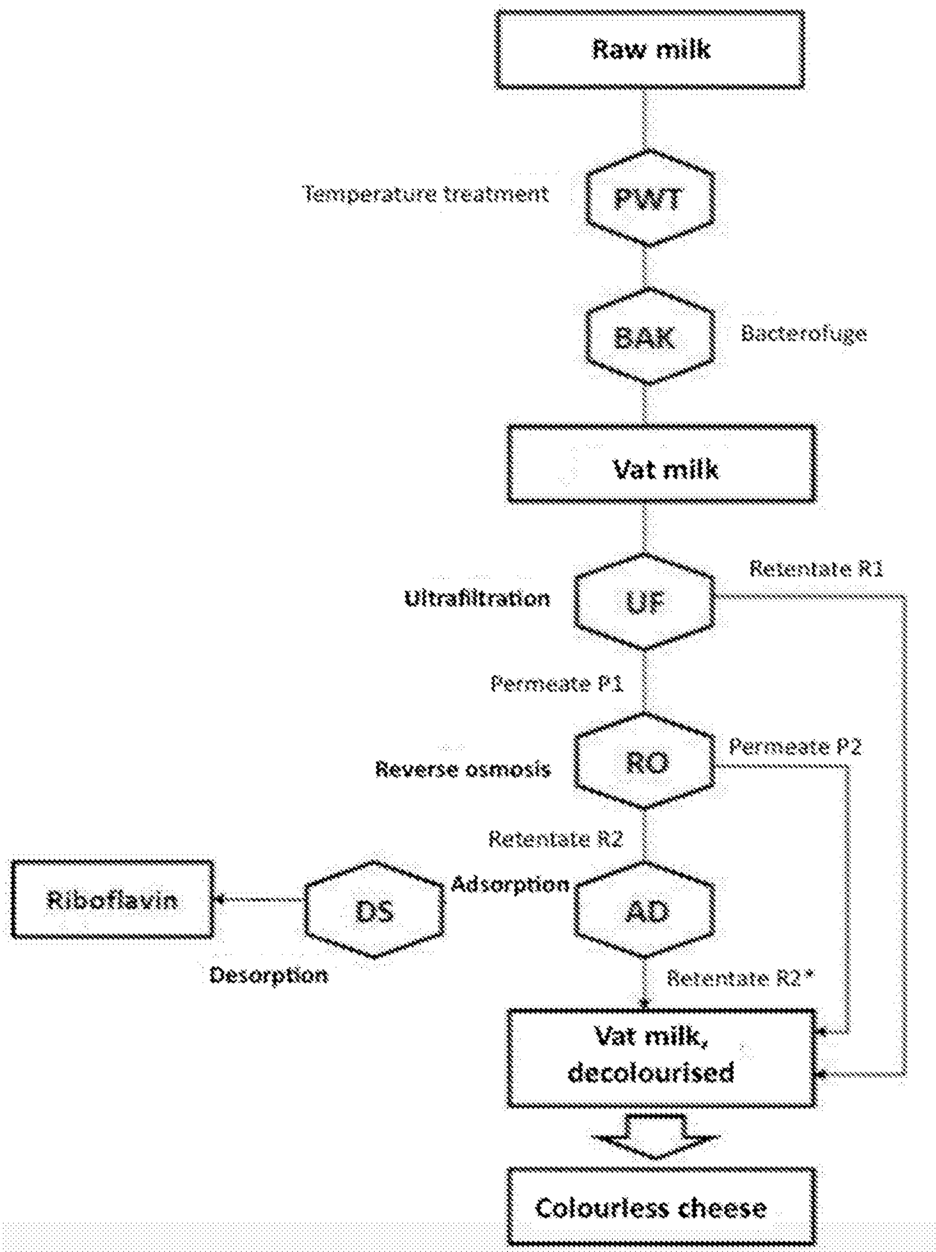


Figure 1

Flowchart showing the production of colourless cheese and isolation of riboflavin