DAIRY PRODUCTS RESEARCH CENTRE

MOOREPARK

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Novel Milk Protein Ingredients

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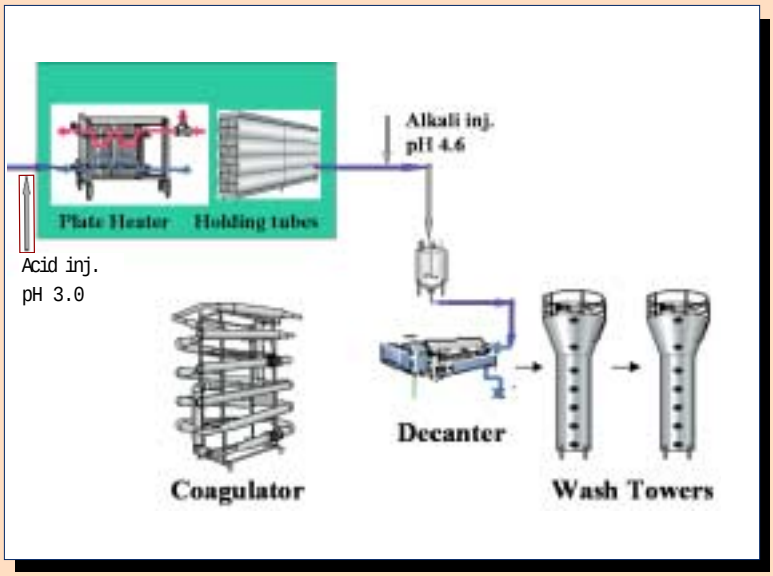
A manufacturing process for the preparation of a novel casein-type product milk proteinate, incorporating casein and whey protein was developed and patented.
A contrasting novel ingredient, based on recovery of casein in its native form (phosphocasein) from milk, was demonstrated using a microfiltration process.This ingredient excelled in terms of acid gelation behaviour, particularly when combined with pre-denatured whey protein.



Development of Ingredient Applications based on Novel Casein/Caseinate Products

(Novel Milk Protein Ingredients)

Armis No. 4520

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Summary and Conclusions

The manufacture of casein/caseinates containing whey protein is immediately attractive due to its potential to enhance product yield. However, some technologies capable of producing these products are ineligible for manufacturing subsidy because of restrictions pertaining to relevant EU regulations. Other emerging technologies require refinement and process design before implementation at industrial level. Furthermore, the implications of incorporating virtually the entire complement of whey protein in what is essentially a caseinate ingredient needs to be investigated carefully in terms of the versatility of use in a wide range of food formulations.

The development is significant in the context of U.S. market changes - traditionally, an important outlet for Irish casein exports amounting to 20,000 - 27,000 t per annum. Ireland accounts for ~ 30% of EU casein/caseinate production with the greater proportion in Rennet form (27,000 t) and the remainder (18,000 t) as Acid casein.

In recent years, a new market for a related casein ingredient - milk protein concentrate (MPC) opened up in the US, and accounted for total imports of 40,000 t in 1998, 10,000 t of which were exported from Ireland. However, this market is more restricted due to regulatory changes introduced in response to the perceived threat of MPC imports to the US dairy industry.

Since casein, or its derivative products such as milk proteinate (EU Annex III compliant), are not perceived to be in competition with local milk supplies and dairy ingredients, it is now hoped that Irish casein manufacturers may be able to reclaim recently lost markets through

the introduction of an innovative proteinate ingredient which is expected to command a premium in nutrition applications e.g. in sports, infant formula and nutraceutical products.

With a choice of emerging new technologies for the production of novel casein-related ingredients, the dairy industry has an opportunity to decide on what is appropriate for the defence of its market share and at the same time benefit from simultaneous compliance with relevant regulatory supports (EU) and market access rules (USA).

Hence the main aims of this project were:

* *To investigate new technologies for the isolation of casein and casein/whey protein combinations in the course of developing new milk protein ingredients, and*

* *To compare the performance in selected food formulations of novel milk protein ingredients namely milk proteinates, milk protein concentrates, native phosphocasein and classical Annex III casein products.*

Main Conclusions and Achievements

* *A manufacturing process for the preparation of a novel casein type product termed milk proteinate was developed and patented. In contrast to traditional processing technology which recovers the major protein group of milk i.e. casein, the new process goes one step further by extracting all the proteins present (namely casein and whey protein).*

The advantages of so doing is that:

- the product satisfies the requirements for EU subsidy for the manufacture of Annex III-grade casein,

- manufacturing yields are increased, and

- a number of interesting properties were established for the resulting product. For instance, proteinate is superior to caseinate as a stabilising ingredient in cream liqueur manufacture.

** Other related casein-based ingredients were prepared using newly-commissioned large pilot scale membrane separation processes based on ultrafiltration (UF), microfiltration (MF) and electrodialysis (ED). The process conditions necessary for the preparation of high protein variants of milk protein concentrates (MPC) and phosphocasein (PC) were identified.*

** Novel phosphocasein ingredients proved versatile during model studies on heat stability and acid gelation. During the course of the latter, it was observed that exceptional gelation behaviour occurred during acidification of phosphocasein/pre-denatured whey protein blends. This provides a basis for the development of highly functional ingredients aimed at yoghurt and fresh cheese manufacture.*

** Considerable industry interest has been expressed in these developments, leading to early technology transfer engagement with a number of parties.*

Research and Results

The project had a number of specific objectives as follows:

* to prepare protein-enriched ingredients based on combinations of casein and whey protein in a variety of forms e.g. by *novel precipitation techniques* (Annex III casein - total milk proteinate; acidified milk proteinate) and *advanced membrane separation processes* (milk protein concentrates, phosphocasein).

* to study the compositional, structural and functional properties of these isolated proteins using established chemical, analytical (HPLC and polyacrylamide gel electrophoresis) and model functionality techniques (viscosity, sensitivity to calcium, stability to alcohol, cream liqueur analogues, etc.).

* to develop the process technologies for pilot scale preparation of milk proteinates, phosphocasein and modified milk protein concentrates. This will be accompanied by compositional analysis of the experimentally produced ingredients.

* to study the acid gelation behaviour of phosphocasein in model systems with a view to ingredient development for applications in yoghurt and fresh cheese.

* to study the stability of concentrated proteins to heat and acid under controlled ionic conditions and examine factors affecting the heat stability of spray dried, reformulated 'milks' prepared using micellar or micellised caseins in combination with non-denatured or pre-denatured whey proteins.

Process development

A 75 litre/h plate heating plant was used as a pilot scale model on which to establish a continuous coagulation (co-precipitation) process based on the principles of the Moorepark-patented proteinate process *(Fig. 1)*. On-line acid dosing was fitted at the point of entry to the heater in order to acidify the skim milk feed to pH 2.3 - 3.5. An on-line alkali dosing system was introduced at the point of discharge from the plant where the cooled acidified milk (55 - 65ºC) was readjusted to its isoelectric point (pH 4.6). The plant was configured to operate at 90ºC with 10 min holding time based on the results of earlier laboratory and batch heating studies. The resulting proteinate curd was separated manually from its whey, and washed twice before neutralisation to ~ pH 7.0 using sodium hydroxide and spray drying. Curd was also dried in the acid form using an attrition drier.

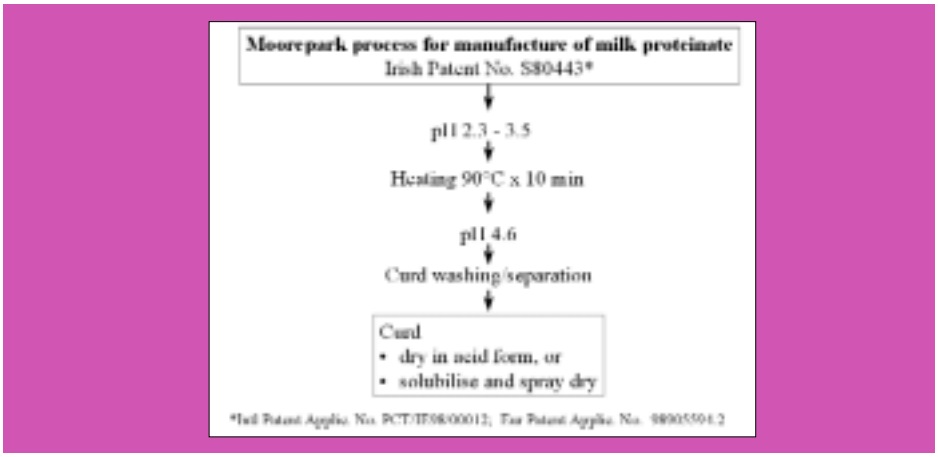

Fig. 1: Outline of key steps in the manufacture of Milk Proteinate according to the Moorepark process.

An extended run time of up to 10 h proved that the process was sufficiently robust for implementation as a continuous industrial operation. Other trials undertaken enabled conditions for curd formation to be optimised.

The process was later scaled up to operate on a larger plate heat exchanger at 500 l/h as a further step in process validation, and also to prepare larger quantities of ingredient for functional evaluation and food formulation application.

Product composition

The composition of the experimentally-produced milk proteinate exceeded *(Table 1)* the specification set out under EU Regulation (EEC) No 2921/90 in respect of the higher protein and lower ash contents achieved. These values illustrated the ease and effectiveness with which a 2-step curd washing enabled the specification to be met.

Table 1. Comparison of the composition of pilot-scale produced milk proteinate with that specified for Annex III caseinates according to EU Regulation (EEC) No 2921/90.

Constituent	Milk Proteinate	Caseinates - Annex III
Fat	1.50	1.50
Protein	91.76	85.00
Lactose	1.00	1.00
Ash	3.51	6.50
Moisture	2.67	6.00

The pH of milk acidification prior to heat treatment was critical to the successful recovery of the whey protein during subsequent processing stages.

Protein recoveries, established after heating (90ºC for individual holding times of 5 and 10 min) acidified milks at different values within the range (pH 2.25 - 3.34) were measured. In the case of the shorter holding time (5 min), protein recoveries varied from 43 to 62% throughout the pH range 2.24 - 3.4. On repeating this work with 10 min holding, protein recovery was generally about the same (48 - 74%), except that there was a clear indication that recovery improved as pH increased. From an operational viewpoint, higher pH values within the range cited caused weaker curd formation. Temperature at the point of final pH correction appears to be important also in terms of curd integrity and possibly protein recovery.

The patented process was now rugged enough to withstand extended run times with > 8 hours continuous coagulation being accomplished in the pilot plant with ease. Although proteinate curd was comparably weaker than that of casein, successful recovery using decanter centrifuges, proved that the process could be successfully exploited during the curd washing/separation stages of industrial casein plants.

The novel ingredient satisfies the requirements of EU Regulations governing the availability of subsidy for the production of Annex III casein/caseinate, both in terms of the technological detail (use of coagulation step) and in compositional specification.

Functional evaluation

In contrast to traditionally-produced co-precipitates, the development of a process for the preparation of milk proteinate marked a major advance in terms of producing a highly soluble and functional protein combination where the presence of whey protein at levels just below its naturally-occurring casein/whey protein ratio in milk could accentuate some distinct properties.

The results of functional tests suggest that milk proteinates are comparable to caseinates in most respects, and perhaps even better in some instances.

Compared to caseinate milk proteinate has:

- Slightly higher viscosity
- Superior foaming
- Almost similar heat stability characterisitcs

Milk proteinates, especially those produced by the Moorepark process, performed better than caseinate in terms of alcohol sensitivity and the cream liqueur analogue test. A slower rate of viscosity increase during storage and lower final viscosity after 60 days was evident (Fig. 2). This clearly sets the ingredient apart from caseinate in terms of its appeal for cream liqueur manufacturers.

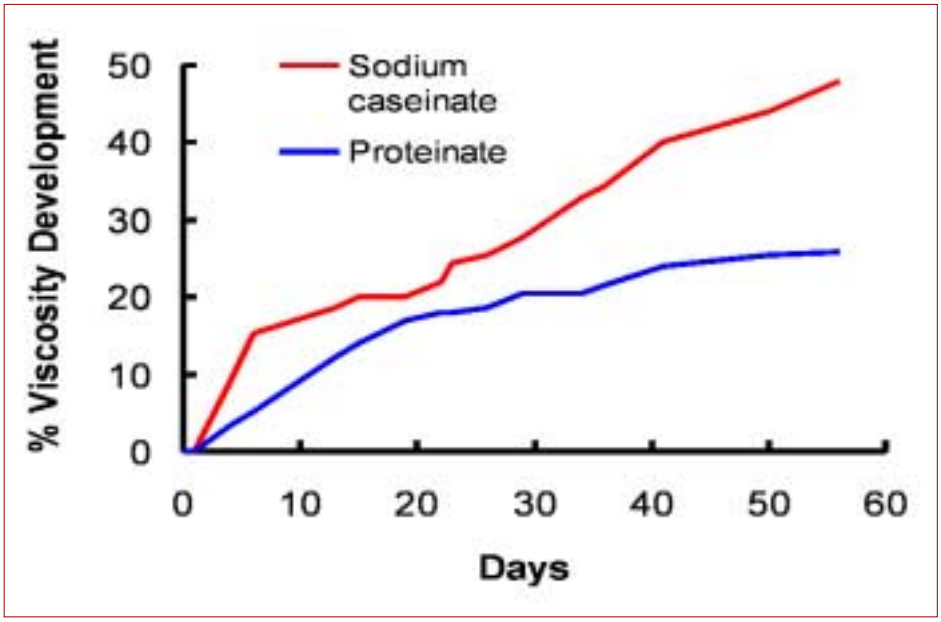

Fig. 2: A comparison of viscosity development in cream liqueur analogue prepared from either milk proteinate or sodium caseinate.

Phosphocasein

Modified MPCs and phosphocasein evolved during the course of the sub-project as micellar-based casein ingredients with distinct functional attributes in contrast to the non-micellar status of solubilised, sodium form of milk proteinate.

Native phosphocasein was prepared from skim milk using a Tetra Pak Alcross™ M, Type 2 x 19 Special, crossflow microfiltration (MF) fitted with a 0.1 µm pore size ceramic membrane with a filtration area of 13.3 m^2. Batch dilution of skim milk (dia-microfiltration) using deionised water before each step of a 2-stage MF process enabled a

spray dried phosphocasein ingredient with a total protein content of ~ 80% to be produced.

Experimentally-produced phosphocasein was notable for its behaviour in model acid gel tests which were set up to simulate yoghurt preparation. The principle technological features of yoghurt manufacture such as protein interaction and acid gelation were featured. The extent to which such interactions affect acid gelation was followed by combining native phosphocasein and whey protein isolate in the approximate ratio that occurs in milk. Again, whey protein was to play a role - this time, when added in the denatured form, increased gelation dramatically during the initial acidification phase and overall gel strength towards the end of fermentation.

Thus, it became apparent that this type of ingredient development brought certain benefits by isolating individual components from milk, modifying them in isolation and achieving a unique functional property following recombination later.

On the strength of the above development, a fresh cheese model was also created to explore the effects of working with an acid gel system using much higher protein concentrations than that of a yoghurt model. Preliminary results are very promising and suggest that novel approaches for the manufacture of fresh cheeses using the above protein ingredients may be possible.

The fresh cheese model was created by means of chemical acidification of 12% (w/w) protein solutions prepared from native phosphocasein, sodium caseinate and whey protein isolate (WPI) in

lactose-free simulated milk ultrafiltrate. The effects of varying the ratios of (i) casein/whey protein, and (ii) phosphocasein/sodium caseinate (on a protein basis) on the rheology of the resulting acid gels were studied in the course of optimising acid gelation conditions and adjustment of composition in line with that of typical fresh cheese.

Some additional work is needed to identify a lower cost source of whey protein for this purpose - the relatively expensive, whey protein isolate (WPI) was used in the course of studies so far. A cheaper whey protein source that would sustain pre-denaturation type treatment would assist in contributing to an improved performance/cost relationship of the resulting innovative ingredient.

Methodology was successfully put in place to quantify the actual amount of whey protein in the co-precipitated proteinate ingredient, the solubility of which was confirmed by nitrogen analysis following reconstitution. Data obtained from SDS gel electrophoresis indicated that little direct binding of whey protein to casein occurs during co-precipitation.

Overall Conclusions

The transformation of a novel milk protein co-precipitation technique from a laboratory concept to a continuously operating process at pilot scale level was successfully demonstrated for the preparation of milk proteinate. Two objectives were accomplished in the course of doing so - the innovative process may now be implemented with certain

adaptations on industrial casein manufacturing plants (as outlined in *Fig. 3*), and operation at large pilot scale level affords sufficient ingredient sample to be produced for market development purposes.

A contrasting novel ingredient based on recovery of casein in its native form (phosphocasein) from milk was demonstrated using a microfiltration process. This ingredient excelled in terms of acid gelation behaviour, particularly when combined with pre-denatured whey protein, and highlights its potential as a base for ingredient innovation as a yoghurt texturiser.

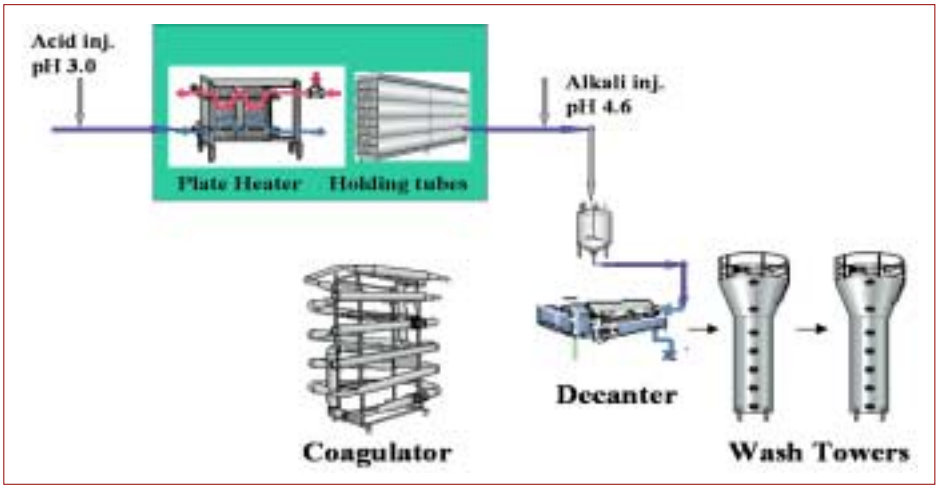

Fig. 3: Adaptation of a casein manufacturing plant for manufacture of milk proteinate.- front-end positioning of a thermal processing step before coagulation. (With acknowledgment to Tetra Pak Dairy Processing Handbook for the use of images to depict individual unit processes).

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