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(54) Title: GEL PRODUCTS AND A PROCESS FOR MAKING THEM

(57) Abstract

A proteinaceous product comprises a stable, substantially clear, thermally irreversible gel formed by the reaction product of protein and reducing sugar, preferably containing from 2 to 25 % gel-forming protein by weight. Particles or pieces of edible material may be embedded in the gel, or the gel may be divided into pieces and incorporated as an ingredient in a food product, and the product can be rendered commercially sterile while remaining substantially clear. Such products can be produced by a process which comprises reacting an aqueous dispersion of a protein or proteinaceous material with a reducing sugar or source thereof in the presence of a denaturing agent (e.g. a chaotropic agent), and/or denaturing conditions (e.g. alkaline pH).

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# GEL PRODUCTS AND A PROCESS FOR MAKING THEM

The present invention relates to novel protein gels and related products and to a process for making them.

It is known that aqueous solutions or dispersions of so-called functional proteins or proteinaceous materials, such as blood plasma, egg albumin or whey protein, can be coagulated by heat to form opaque solid gels which are thermally irreversible. It is also known that other proteins, for example gelatine, can form clear but thermally reversible gels.

The present invention in one aspect now provides a stable, substantially clear, thermally irreversible gel formed by the reaction product of protein and reducing sugar. Furthermore, it is possible to dry a sheet of the solid gel to form a clear film, which may have a variety of applications in place of existing film materials.

Surprisingly, gels formed by this invention retain their clarity, even after substantial further heat processing or other treatment to render them commercially sterile, and for this reason may be described as 'stable'.

By a "substantially clear" gel is here meant a gel which, but for the possible inclusion of extraneous heterogeneous components, is essentially transparent in that light can pass therethrough without substantial scattering or dispersion by the gel-forming protein content. The gels may be substantially colourless or coloured, depending upon the starting materials and the reaction conditions, if only by reason of a Maillard type reaction between the protein or associated aminoacids and the sugar.

It will be appreciated that, if the gel has a deep colour, it may not give the appearance of transparency to a casual observer owing to absorption of light, but yet, by the low level of scattering, be substantially clear within the meaning of this term intended here. By way of example, transmission of light at appropriate wavelengths can be used to estimate the degree of clarity or transparency of gels. This is illustrated in Example 9 below.

In accordance with another aspect of this invention, a process for producing a gelled aqueous phase comprises reacting an aqueous solution or dispersion (hereinafter referred to as a "dispersion") of a protein or proteinaceous material with a reducing sugar or source thereof in the presence of a denaturing agent and/or denaturing conditions and forming therefrom a substantially clear, thermally irreversible gel structure.

It is contemplated that any protein may be employed that is capable of solubilisation in aqueous dispersion and can be formed by heat or the lapse of time into a gel structure under the conditions of the present invention. The preferred proteins, especially where a solid gel is required, are globular proteins such as blood plasma, whey protein or egg albumin but it may be acceptable to use other proteins such as plant storage proteins (e.g. soya), casein, mycoprotein or muscle proteins. For commercial applications it is desirable to use cruder forms of protein, for example crude blood plasma, fish offal or yeast, rather than expensive purified proteins such as bovine serum albumin or lactoglobulin.

The concentration of the functional protein in the aqueous dispersion may vary with the type of product required and the purity or functionality of the protein, but is preferably in the range of 2-25% by weight of the dispersion. Most commonly, the protein concentration will be in the range of 4-15% but for gels produced from purified proteins may be as low as 2%, while for crude, less active protein materials may be as high as 25%.

The reducing sugar may be any sugar capable of entering into a Maillard reaction. Examples include lactose, xylose and glucose. For commercial applications it may be desirable to use crude source of reducing sugar such as whey powder rather than expensive purified sugars such as lactose. Nevertheless, certain purified sugars such as xylose are effective at such low concentrations that they may be economically competitive in commercial applications.

The reducing sugar concentration is preferably in the range of 1-6% by weight of the aqueous dispersion but for purified materials may be as low as 0.3% and for crude sugar sources may be as high as 10% by weight.

The protein denaturant employed may be selected from a range of chaotropic denaturants such as sodium dodecyl sulphate, guanidinium hydrochloride and the like. A range of protein denaturing conditions is also available such as adjustment of pH, of ionic strength, application of heat and application of pressure. These conditions and denaturant agents may be used singly or in combination. A protein denaturant modulator such as simple salts eg. potassium chloride, sodium chloride or sodium citrate, may also be employed to effect modulation of the degree of denaturation caused by the protein denaturant and/or the denaturing conditions. Clearly, any additive used for this purpose must be acceptable in the intended product.

Where alkalinity is used to achieve denaturing conditions, the aqueous dispersion will be converted into a substantially clear, thermally reversible gel at a rate dependent upon the temperature of the dispersion, the concentrations of the protein and reducing sugar reactants, and conditions such as pH value. At high concentrations of the reactants, the gel will form at room temperature over a number of hours, whereas with average concentrations heating may be necessary. For example a temperature of, say, 80°C may suffice, but other elevated temperatures including pasteurization or sterilization temperatures are effective.

During the course of the reaction the pH of the aqueous dispersion may be observed to fall so that where the initial pH of the mixture is, for example, about 12, the pH of the final gel product will usually be in the neutral range, say pH 6-8. This permits its use in food applications where highly alkaline products would be unacceptable. For food uses it is preferred to raise the alkalinity of the dispersion to an initial pH 10-13, preferably by the addition of potassium hydroxide, although other monovalent alkaline hydroxides and salts can be used.

It will be frequently found, particularly with the cruder protein forms, that reducing the strength of the ionic environment of the protein leads to an easier denaturation of the protein under the influence of a denaturant and/or denaturing conditions. For example, removal of salt from the proteins employed can reduce the alkaline pH value needed to achieve a

stable, clear gel and, in some cases, the heat employed in processing may then suffice without pH adjustment.

However, in some situations, particularly but not necessarily with the purer protein forms, the protein molecules may already under mild denaturing conditions be in a very substantially denatured form. In this situation the addition of a certain amount of a protein denaturing modulator e.g. sodium chloride, may be necessary to reduce the charges on the protein molecules to reduce the distention of the molecules so that on addition of a reducing sugar easier crosslinking may occur, leading to a heat stable transparent protein gel network. Thus under some denaturing conditions certain proteins may fail to gel until a certain level of salt strength has been incorporated prior to crosslinking. At higher levels of sodium chloride further repression of denaturation occurs prior to crosslinking and weaker, poorer gels may be obtained.

Whilst not wishing to be bound by the following hypothesis the inventors believe that the invention involves denaturing the protein so as to unfold the molecules by applying a denaturant and/or denaturing conditions. The application of a reducing sugar then results in the formation of crosslinks between the protein molecules leading to a transparent, heat stable, thermo-irreversible gel, when optionally the denaturing conditions may be removed. This cross linking, before protein aggregation occurs, gives rise to clear, heat stable gels and avoids the otherwise formation of opaque aggregated protein gels.

Important among the applications of this invention is the production of food products in which particles or pieces of edible material are embedded in a gel medium, especially commercially food products such as meat-in-jelly canned products. In the preparation of such products it may be convenient to use the normal heat sterilisation procedure to induce the conversion of the aqueous dispersion into the required gel.

By virtue of the clarity of the gel, the typical surface appearance of pieces of meat embedded in the gel is apparent upon visual inspection of the product. More particularly, it is preferred that the clarity of the gel should be such that the surface appearance of meat remains visible when coated with a

layer of the gel 2.5 mm in thickness. The glossy character of the gel is also of advantage in a meat-in-jelly product, glossiness in this context referring to the lustre of the gel surface, which may be considered as exhibiting a relatively high level of specular reflectance.

Another use of the thermally irreversible gels of this invention is in the production of discrete pieces or chunks of edible material for inclusion in a canned product, serving for example as a binder for nutritive ingredients. Such pieces can be formed by conventional techniques and pass unchanged through retorting processes .

The aqueous dispersion of the reactants for a gel of this invention has good emulsifying properties, and this permits the emulsification of added oils or fats before the reaction to form the gel product. This enables stable, low calorie spreads to be produced.

Another group of applications of this invention employs the gel as a heat-resistant substitute for gelatine, for example in products for use in high temperature climates and in the preparation of hallal food products.

Sheets of the gel can be produced, for example, by spreading the aqueous dispersion on a temporary support before formation of the gel. Such sheets can be dried to form clear protein films with a variety of uses. The flexibility of such films can be enhanced by incorporating a plasticizer such as glycerol in the initial dispersion.

Formation of a protein film in situ can be used to provide an edible coating on a variety of food products. For example if a coating of the aqueous dispersion is applied to fruit or vegetables and allowed to gel before being dried, an edible protective barrier is provided on the foodstuff. Other products on which similar coatings may be useful include chocolate bars or materials which are normally sticky to the touch or dangerous to handle. Such a film coating can also be used as a fat barrier layer during the frying of potato chips or as a barrier to migration of moisture into pastry in, for example, custard tarts.

The following are examples of the practice of this invention:

Example 1

1Kg frozen blood plasma

30g whey powder

The plasma is thawed and the whey powder added and mixed thoroughly. The pH is adjusted to 12 by the dropwise addition of a 30% w/v aqueous solution of potassium hydroxide and the mixture heated to 125°C for 10 minutes. A clear, bright, glossy brown gel of pH 7 is produced.

Example 2

The same ingredients are used as in Example 1. The alkaline mixture is combined with meats or meat analogues in a can, and processed at 129°C for 1 hour. The product consists of cooked meats in a glossy, clear, brown gel, at pH 7.

Example 3

1Kg frozen blood plasma

35g whey powder

0.1 ml lactase

The same method as Example 1 is used, except that the enzyme is added to the plasma and whey, to break down the lactose into the more readily reactive glucose and galactose, and the mixture is incubated at room temperature for 2 hours prior to pH adjustment.

Example 4

10g of dried plasma powder and 1g of xylose, glucose or lactose are added to 100g of water. The mixture is dispersed using a high shear homogeniser. The pH of the mixture is adjusted to pH 12 with KOH or NaOH. The mixture is divided into 20 ml aliquots in screw capped vials and the samples are autoclaved at 125°C for 15 minutes. The product is a glossy, clear, dark brown gel of pH 6.5-7.5.

Example 5

Samples of gel prepared in accordance with Example 4 were placed in a freezer at -18°C for 1 hour. The frozen samples were allowed to thaw at room temperature. The samples were essentially the same before and after freezing. This demonstrates that gels according to this invention can exhibit freeze-thaw stability.

Example 6

A clear gel is formed as in Examples 1, 3 or 4 optionally containing dispersed edible material such as meat slurry, is divided into pieces and added as an ingredient to a raw meat mixture. This is canned and conventionally sterilised to produce a cooked meat product containing pieces of gel which have remained clear, glossy and thermo-irreversible.

Example 7

15g plasma powder and 2g xylose are added to 100ml of water together with 1.3g of sodium tripolyphosphate (STPP) and 0.2g sunflower oil. The mixture is homogenised using a high shear mixer. The pH of the mixture is adjusted to 12 with KOH. The mixture is allowed to stand at room temperature for 4 hours or more, by which time the product has set to form a light brown jelly. The product can be canned and autoclaved at 129°C for 1 hour, producing a substantially clear gel. The gel phase itself retains its clarity, although this may be reduced slightly by virtue of the suspended oil or fat.

Example 8

An aqueous suspension of 10% plasma powder, 2.5% xylose and 2.5% sodium dodecyl sulphate (SDS) is heated to 125°C for 10 minutes. A clear red/brown heat irreversible gel is formed.

Example 9

The following example demonstrates the effectiveness of pH modification in achieving the objects of this invention. It also illustrates the use of light transmission to estimate the degree of clarity or transparency of gels.

An aqueous suspension of 10% plasma powder and 2% lactose was divided into two aliquots. One portion was adjusted to pH 12 with 1M sodium hydroxide, the other remained at pH 8. Each was added to a 1mm cuvettes via a syringe and heated to 121°C for 2 minutes.

The mixture without pH modification gave an opaque, heat irreversible gel which transmitted less than 1% of light in the 400 to 800nm region.

The mixture adjusted to pH 12 gave a clear heat stable gel with up to 70% transmittance of light in the 400 to 800nm region.

Example 10

100 ml of whole citrated blood is mixed with 3g of glucose and the pH adjusted to 12 with 1M NaOH. It is heated to 125°C for 15 minutes to produce a robust dark brown glossy gel.

Example 11

15g whole blood powder and 3g lactose are dispersed in 100ml of water, and the pH adjusted to 12 with 1M KOH. The mixture is heated to 130°C for 5 minutes to yield a robust dark brown glossy gel.

Example 12

100g of minced white fish offal is homogenised with 3g of galactose, and the pH of the mixture adjusted to 11.5 with 1M NaOH. This is heated to 125°C for 15 minutes to produce a heat irreversible clear brown gel containing pieces of white fish.

Example 13

The procedure of Example 4 is repeated with 9g of egg albumin powder replacing the dried plasma. A similar gel is obtained.

Example 14

A 10% solution of dried and powdered egg albumen is prepared in distilled water. The solution is dialysed in distilled water for 24 hours. The solution is centrifuged at 1400 rpm in a Beckman J21C centrifuge (JA-14 rotor) for 15

minutes. The supernatant is retained for use. The solution has a pH of approx. 6.6.

0.5% xylose is added to the solution, which is then processed for 30 minutes at 90°C and then cooled. The solution is then retorted at 125°C for 15 minutes. The end product is a firm, elastic and clear orange gel with a pH of approximately 6.4.

Example 15

A 10% solution of an ultrafiltered and dried porcine plasma preparation is made up in distilled water. 0.5% xylose is added to the solution, and portions of this mixture are adjusted to pH 10.2, pH 10.9 and pH 12.0. Different levels of sodium chloride are then added to portions of the pH-adjusted aliguots. The samples are retorted at 125°C for 15 minutes.

At pH 10.2 a clear brown gel is formed. At pH 10.9, a clear gel is formed at 30mM salt. At pH 12.0 a clear liquid is formed at 30mM salt, a clear gel at 150mM and a soft translucent jelly at 500mM.

CLAIMS

1. A proteinaceous product comprising a stable, substantially clear, thermally irreversible gel formed by the reaction product of protein and reducing sugar.

2. A proteinaceous product according to claim 1 comprising a protein gel containing from 2 to 25% gel-forming protein by weight.

3. A proteinaceous product according to claim 1 or 2 in which the gel-forming protein is a globular protein.

4. A proteinaceous product according to any of claims 1 to 3 which comprises particles or pieces of edible material embedded in the gel.

5. A proteinaceous product according to any of claims 1 to 4 in which the gel is divided into pieces and incorporated as an ingredient in a food product.

6. A proteinaceous product according to any preceding claim in which oil or fat is dispersed in the gel.

7. A proteinaceous product according to any preceding claim which is rendered commercially sterile while remaining substantially clear.

8. A proteinaceous product according to claim 1, 2 or 3 in the form of a protein film obtained by drying the protein gel.

9. A proteinaceous product according to claim 8 in which the protein film constitutes an edible coating or barrier layer on a foodstuff or other product.

10. A process for producing a proteinaceous product according to claim 1 which comprises reacting an aqueous dispersion of a protein or proteinaceous material with a reducing sugar or source

thereof in the presence of a denaturing agent and/or denaturing conditions, and forming therefrom a substantially clear thermally irreversible gel.

11. A process according to claim 10 in which the gel structure comprises from 2-25% gel-forming protein by weight.

12. A process according to claim 10 or 11 in which the protein is a globular protein.

13. A process according to any of claims 10 to 12 in which the reducing sugar is lactose, xylose or glucose or a source thereof, and is present in a concentration of from 0.3-10% by weight of the aqueous dispersion.

14. A process according to any of claims 10 to 13 wherein the denaturing agent is an alkali.

15. A process according to any of claims 10 to 13 wherein the denaturing agent is a chaotropic agent.

16. A process according to any of claims 10 to 15 in which the salt content of the protein or proteinaceous material is reduced prior to gel formation.

17. A process according to any of claims 10 to 16 in which particles or pieces of edible material are mixed with the aqueous dispersion and other reactants prior to formation of the gel.

18. A process according to any of claims 10 to 17 in which the gel is divided into pieces and incorporated in a food product.

19. A process according to any of claims 10 to 18 in which the aqueous dispersion containing the other reactants and any additional components of the final product is subjected to pasteurizing or sterilizing conditions.

20. A process according to any of claims 10 to 19 in which oil

or fat is emulsified in the aqueous dispersion prior to formation of the gel or thickened phase.

21. A process according to any of claims 10 to 16 in which the aqueous dispersion containing the other reactants is spread on a temporary support and dried to form a protein film.

22. A process according to claim 21 in which a plasticizer is incorporated with the aqueous dispersion.

23. A process according to any of claims 10 to 16 in which the aqueous dispersion containing the other reactants is coated on a foodstuff or other product and dried thereon to constitute a coating or barrier layer.

# INTERNATIONAL SEARCH REPORT

PCT/GB 92/00736

International Application Nc

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 A23J3/00; A23L1/05; A23L1/056; A23L1/227
A23P1/08

## II. FIELDS SEARCHED

Minimum Documentation Searched[7]

| Classification System | Classification Symbols |
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| Int.Cl. 5 | A23L ; A23J ; A23C ; A23P |

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

## III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

| Category ° | Citation of Document,[11] with indication, where appropriate, of the relevant passages[12] | Relevant to Claim No.[13] |
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## IV. CERTIFICATION

| Date of the Actual Completion of the International Search | Date of Mailing of this International Search Report |
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| 03 AUGUST 1992 | 11.08.92 |
| **International Searching Authority** | **Signature of Authorized Officer** |
| EUROPEAN PATENT OFFICE | VUILLAMY V.M.L. |

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

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| III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET) | | |
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# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. GB 9200736 SA 58669

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 03/08/92
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