FORM 1

REGULATION 9

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

We, SOCIETE DES PRODUITS NESTLE S.A., a Swiss body corporate of Vevey, Switzerland, hereby apply for the grant of a Standard Patent for an invention entitled:-

"PRODUCTION OF HYDROLYSED PROTEINS"

which is described in the accompanying Complete Specification.

Details of basic application:-

Number: 07/258191

Country: United States of America

Date: 14th October, 1988

Our address for service is: SHELSTON WATERS
55 Clarence Street
SYDNEY, N.S.W. 2000.

DATED this 6th Day of October, 1989
SOCIETE DES PRODUITS NESTLE S.A.

by .....

Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

To: The Commissioner of Patents
WODEN A.C.T. 2606

File: D.B. S-128

Fee: $213.00

SO10611 06/10/89

CONVENTION APPLICATION BY A COMPANY

FORM 8 - REGULATION 12 (2)

AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made by

(a) Here Insert (in full) Name of Company.

(a) SOCIETE DES PRODUITS NESTLE S.A.

(hereinafter referred to as "Applicant") for a patent for an invention entitled:

(b) Here insert Title of Invention.

(b) Production of hydrolysed proteins

(c) and (d) Here Insert Full Name and Address of Company Official authorised to make declaration.

I, (c) Andrzej W. LEDZION

of (d) En la Priauraz, 1807 BLONAY, Switzerland

do solemnly and sincerely declare as follows:

1. I am authorised by Applicant to make this declaration on its behalf.

2. The basic Application(s) as defined by section 141 of the Act was / were made

(e) Here insert Basic Country followed by date of Basic Application.

(f) Here Insert Full Name(s) of Applicant(s) in Basic Country.

in (e) the United States of on the 14th day of October 1988

by (f) America

in ..... on the ..... day of 19

by Paul-Emile CORNET

in ..... on the ..... day of 19

by Rebecca Shu-Chun SO

in ..... on the ..... day of 19

by John Stuart TANDY

(g) Here Insert (in full) Name and Address of actual Inventor or Inventors.

3. (g) Paul-Emile CORNET, of 4, Lafayette Court, GREENWICH, CT 06830, USA, Rebecca Sui-Chun SO, of 32, Sherwood Drive, NEW MILFORD, CONNECTICUT, 06776, USA, John Stewart TANDY, of 207A, Blue Swamp Road, LITCHFIELD, CONN 06759, USA, Roland FAESI, Swiss Citizen, Sæntisstrasse 1A, 8311 BRUETTEN, SWITZERLAND, Milo A. NIELSEN, United States Citizen, 17520 Orna Drive Granada Hills California 91344 USA ..... is/are the actual Inventor(s) of the invention and the facts upon which Applicant is entitled to make the Application are as follows:

See reverse side of this form for guidance in completing this part.

The applicant would be entitled to have assigned to it a patent granted to any of the actual inventors in respect of said invention.

4. The basic Application(s) referred to in paragraph 2 of this Declaration was/were the first Application(s) made in a Convention country in respect of the invention, the subject of the Application.

DECLARED at Vevey, Switzerland

this 18th day of October, 1991

(h) Personal Signature of Declarant (c) (no seal, witness or legalisation).

(h)

(12) PATENT ABRIDGMENT (11) Document No. AU-B-42631/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 619600

(54) Title
PRODUCTION OF HYDROLYSED PROTEINS

International Patent Classification(s)
(51)[4] A23J 001/12 A23J 001/00 A23J 001/14 A23J 001/20
(51)[5] A23J 003/00 A23J 003/32

(21) Application No. : 42631/89 (22) Application Date : 06.10.89

(30) Priority Data

(31) Number (32) Date (33) Country
258191 14.10.88 US UNITED STATES OF AMERICA

(43) Publication Date : 26.04.90

(44) Publication Date of Accepted Application : 30.01.92

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(56) Prior Art Documents
US 4759944
US 4798736

(57) Claim

1. A process for the production of a hydrolysed protein which comprises hydrolysing a plant or animal protein with hydrochloric acid to give a slurry and then, before or after filtering off the residual unhydrolysed material, treating with alkali to a pH of from 8 to 14 and holding at a temperature and for a period of time to reduce the amount of undesirable chlorinated compounds and readjusting to a pH of from 4 to 7 to give a liquid hydrolysed protein filtrate.

5. A process according to claim 1 wherein the temperature of the hydrolysis is from 70°C to 140°C.

619600

COMMONWEALTH OF AUSTRALIA

FORM 10

PATENTS ACT 1952

COMPLETE SPECIFICATION

FOR OFFICE USE:

Class Int.Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

Name of Applicant: SOCIETE DES PRODUITS NESTLE S.A.

Address of Applicant: Vevey, Switzerland

Actual Inventor: Paul-Emile Cornet, Rebecca Sui-Chun So and John Stewart Tandy

Address for Service: SHELSTON WATERS, 55 Clarence Street, Sydney

Complete Specification for the Invention entitled:

"PRODUCTION OF HYDROLYSED PROTEINS"

The following statement is a full description of this invention, including the best method of performing it known to us:-

Abstract

Production of hydrolysed proteins

A process for the production of a hydrolysed protein which comprises hydrolysing a plant or animal protein with hydrochloric acid to give a slurry and then, before or after filtering off the residual unhydrolysed material, treating with alkali to a pH of from 8 to 14 and holding for a period of time to reduce the amount of undesirable chlorinated compounds and readjusting to a pH of from 4 to 7 to give a liquid hydrolysed protein filtrate.

The present invention relates to a process for the production of hydrolysed proteins.

Hydrolysed proteins have been known in food systems for centuries in the Far East in the form of soy sauce which traditionally has been prepared by enzymatic hydrolysis requiring a long period of time, usually several months, for preparation.

About 100 years ago, a more rapid method of hydrolysing proteins for producing flavours was developed using hydrochloric acid in which the time required is only a few hours. In this acid hydrolysis process, vegetable plant or animal proteins derived from corn, soy, wheat, rice, yeast, peanut or casein are commonly used as starting protein sources and are usually obtained as a result of the separation of the protein fraction during milling of grains or following solvent extraction of oils. The protein contents of these raw materials may range from 40% to 90% with a general average of about 60%. Normally, the protein source is hydrolysed with hydrochloric acid having a concentration of about 20% by weight at a temperature from about 120° - 135°C over a period from about 5 to 8 hours and elevated pressure up to 30 psig (2 bars). Following hydrolysis, the slurry is neutralised with a suitable alkaline material such as sodium hydroxide or sodium carbonate to a pH from 5.0 to 5.3 and the residual unhydrolysed material (lignin, humin) filtered out. The slurry may be decolourised prior to filtration or the filtrate following filtration may be decolourised by conventional means e.g. activated carbon, absorption resins. Following filtration of the unhydrolysed material, the dilute liquid can be concentrated to precipitate part of the salt formed and then refiltered. Afterwards, the liquid which contains about 42% solids may be further concentrated to pastes or dried by any conventional means such as spray drying or vacuum drum drying to powdered products. Thus acid hydrolysed proteins can be in either

liquid, paste or powder form and are composed mainly of amino acids and salt resulting from the acid catalysed breakdown of peptide bonds present in edible proteinaceous materials. The flavour of the product will, of course, vary depending upon the type of source of protein used as the raw material.

However, the use of hydrochloric acid in the hydrolysis of proteins leads to the formation in side reactions of certain undesirable chlorinated by-products such as α-chlorohydrins. There are various possible processes which may be considered for reducing the quantities of these compounds. For instance, it would be possible to use a starting material which does not contain any fats, since glycerol is one of the precursors which enables chlorohydrins to be formed with hydrochloric acid. However, on the one hand, starting materials such as these are more or less commercially unobtainable and, on the other hand, would significantly modify the organoleptic qualities of the flavour. In another possibility, hydrolysis could be carried out with a chlorine free mineral acid such as sulfuric acid or phosphoric acid. However, such a modification of the traditional process would also have adverse affects upon the organoleptic qualities of the flavour obtained.

We have developed a process for the production of hydrolysed proteins using hydrochloric acid in which the quantity of undesirable chlorinated compounds is substantially reduced without having a substantial adverse effect on the organoleptic characteristics of the hydrolysed protein product and wherein a flavour may be achieved which is substantially similar to that of a hydrolysed protein produced under normal conditions.

Accordingly, the present invention provides a process for the production of a hydrolysed protein which comprises hydrolysing a plant or animal protein with hydrochloric

acid to give a slurry and then, before or after filtering off the residual unhydrolysed material, treating with alkali to a pH of from 8 to 14 and readjusting to a pH of from 4 to 7 to give a liquid hydrolysed protein filtrate. Afterwards, the liquid hydrolysed protein filtrate may be concentrated to precipitate some of the salt formed and refiltered to give a liquid hydrolysed protein product.

The plant or animal protein may be derived from various origins such as corn, soy, wheat, rice, yeast, peanut or casein and is usually obtained by separation of the protein fraction during milling of grains or following solvent extraction of oils. For example, it is possible to use oil seed cakes, cereal gluten or defatted soya flour.

The hydrochloric acid used for the hydrolysis is preferably concentrated and may have a concentration from 15% to 25%, preferably from 16% to 22% and especially from 17% to 19% by weight. The amount of protein material may vary widely for instance, from 30 to 50% by weight, but more usually from 35 to 45% by weight and preferably from 38 to 42% by weight based on the total weight of hydrolysis mixture.

The temperature of the hydrolysis may be from 70°C to 140°C, more usually from 100°C to 130°C, preferably from 105°C to 120°C and especially from 110°C to 115°C.

The duration of the hydrolysis may vary from 2 to 12 hours more usually from 2.5 to 8 hours, generally longer periods of time being required at lower temperatures. Advantageously, the duration of the hydrolysis is from 3 to 7 hours, especially from 3 to 5 hours.

We have found that by decreasing either the acid concentration from the normal 20% to about 18%, the temperature from the normal 120°C-135°C to 110°C-115°C or the duration from the normal 5-8 hours to 3-4 hours, or a combination

of two or more of these processing parameters, the amount of the undesirable chlorinated compounds can be reduced significantly.

The hydrolysis may be carried out with stirring and, if desired, under elevated pressure for instance up to 100 psig and more usually from 10 to 50 psig.

After hydrolysis, before or after filtering off the residual unhydrolysed material, the hydrolysed protein is first treated with a food-acceptable strong alkali such as KOH or NH_4OH, but preferably NaOH and/or Na_2CO_3 to adjust the pH to from 8 to 14 and held at a temperature and for a period of time to reduce the amount of undesirable chlorinated compounds. The pH is preferably adjusted to from 9 to 13 and especially from 10 to 12 by the alkaline treatment. Generally alkaline treatments to higher pH values require shorter processing times than treatments to lower pH values because the higher the concentration ratio of (OH^-) to the α-chlorohydrin, the faster the reaction and the greater will be the reduction in quantity of the α-chlorohydrin. In addition, at any particular pH the higher the temperature employed, the shorter the time necessary. For example, the temperature may range from ambient to 170°C or even higher if extremely short processing times are used. The time period may range from a few seconds at high pH and temperatures above ambient, to 24 hours or even several weeks or more at ambient temperatures. The actual processing time and the temperature at any given pH is dictated by the residual quantity of undesired chlorinated product and the overall desired organoleptic acceptance of the hydrolysed protein. For example, a high temperature short time treatment such as from 100° to 140°C over a period of from 1 to 5 minutes may be advantageous. The pH of the alkaline hydrolysed protein is then readjusted to a pH from 4 to 7 preferably from 5 to 5.5, with acid,

usually hydrochloric acid at a temperature usually from 10°C to 50°C and preferably from 20°C to 30°C although higher or lower temperatures may be employed.

The residual unhydrolysed material consisting mainly of lignin and humin is filtered off from the slurry before or after the pH adjustment. The slurry may be decolourised prior to filtration or the liquid filtrate following filtration may be decolourised by conventional means e.g. activated carbon, absorption resins. The liquid hydrolysed protein filtrate may then be concentrated, for instance, by evaporation to precipitate some of the salt formed and then refiltered to remove this precipitated salt to give a liquid hydrolysed protein product which may contain from 20% to 50%, and preferably from 35% to 45% by weight of solids. The liquid hydrolysed protein product may then be evaporated further to give a paste of about 85% by weight of solids and, if desired, the paste may be dried and ground to give a powder usually containing about 96-98% by weight of solids.

The following Examples further illustrate the present invention:

Example 1

100 kg of corn gluten containing about 60% protein is hydrolysed with 180 kg of 20% hydrochloric acid at 120°C for 7 hours. The resultant slurry is filtered to remove unhydrolysed material such as lignin and humin, decolourised with active carbon, and the liquid filtrate is then treated with sodium hydroxide solution to a pH of 11.5 and held at the times and temperatures indicated in the following Table I which gives the α-chlorohydrin content as a percentage. The pH is then readjusted to 5.2 with hydrochloric acid at 25°C and the liquid hydrolysed protein filtrate is then concentrated by

evaporation to precipitate some of the salt formed and refiltered to give a liquid hydrolysed protein product having a solids content of 42% by weight. The product has a more rounded, less acidic character when compared with a product prepared by the normal process.

TABLE I

Time (hrs)	35°C	45°C	55°C
0.00	100.00	100.00	100.00
0.25	58.01	33.78	34.69
0.50	0.41	ND	0.04
0.75	0.30	0.10	ND
1.00	0.19	0.07	ND
2.00	0.04	0.07	ND
3.00	0.03	ND	ND
4.00	0.02	ND	ND

It can be seen that increased holding temperatures and times lead to a greater reduction in the quantity of α-chlorohydrin, and that at higher temperatures, shorter times may be used to obtain a specific reduction in the quantity of -chlorohydrin. (ND = not detected)

Example 2

The procedure in Example 1 was repeated except that the liquid filtrate treated with sodium hydroxide was held at 24°C for 14 hours at the pH values indicated in Table II which indicates the percentage α-chlorohydrin content compared with a control at a pH of 5.47.

TABLE II

pH	∝-chlorohydrin %
5.47	100.00
8.24	88.76
9.01	78.77
9.23	68.25
9.47	50.22
9.96	13.05
10.25	4.79
10.43	ND
10.95	ND

Example 3

The procedure in Example 1 was repeated except that the hydrolysis was carried out with 18% hydrochloric acid at 110°C for 3.5 hours and the liquid filtrate treated with sodium hydroxide solution to a pH of 11.5 was held at 35°C for 15 minutes. The flavour of the product was found to be very similar to normally prepared hydrolysed plant proteins. The ∝-chlorohydrin content was so low as to be undetectable.

Example 4

The procedure in Example 1 was repeated except that the hydrolysis was carried out with 18% hydrochloric acid at 120°C for 7 hours and the liquid filtrate treated with sodium hydroxide solution to a pH of 10.5 and held at 120°C for 3.5 minutes. The ∝-chlorohydrin content of the product was less than 0.50 ppm.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A process for the production of a hydrolysed protein which comprises hydrolysing a plant or animal protein with hydrochloric acid to give a slurry and then, before or after filtering off the residual unhydrolysed material, treating with alkali to a pH of from 8 to 14 and holding at a temperature and for a period of time to reduce the amount of undesirable chlorinated compounds and readjusting to a pH of from 4 to 7 to give a liquid hydrolysed protein filtrate.

2. A process according to claim 1 which comprises concentrating the liquid hydrolysed protein filtrate to precipitate some of the salt formed and refiltering to give a liquid hydrolysed protein product.

3. A process according to claim 1 wherein the concentration of the hydrochloric acid is from 15% to 25% by weight.

4. A process according to claim 1 wherein the concentration of the hydrochloric acid is from 17% to 19% by weight.

5. A process according to claim 1 wherein the temperature of the hydrolysis is from 70°C to 140°C.

6. A process according to claim 1 wherein the temperature of the hydrolysis is from 110°C to 115°C.

7. A process according to claim 1 wherein the duration of the hydrolysis is from 2.5 to 8 hours.

8. A process according to claim 1 wherein the duration of the hydrolysis is from 3 to 5 hours.

9. A process according to claim 1 wherein the hydrolysis is carried out under elevated pressure up to 100 psig.

10. A process according to claim 1 wherein the pH is adjusted with NaOH and/or $Na_2 CO_3$.

11. A process according to claim 1 wherein the pH is adjusted to a value from 10 to 12.

12. A process according to claim 1 wherein the slurry is held at the adjusted pH at a temperature from ambient

to 170°C for a period of from several weeks to a few seconds.

13. A process according to claim 1 wherein the slurry is held at the adjusted pH at a temperature from 35°C to 55°C for a period of from 30 minutes to 4 hours.

14. A process according to claim 1 wherein the slurry is held at the adjusted pH at a temperature from 100°C to 140°C over a period of from 1 to 5 minutes.

15. A process according to claim 1 wherein the pH is readjusted to a value from 5 to 5.5.

16. A process according to claim 15 wherein the temperature is from 10°C to 50°C.

17. A process according to claim 2 wherein the liquid hydrolysed protein product is further evaporated to give a paste, which may be dried and ground to a powder.

18. A process for the production of a hydrolysed protein as defined in claim 1 and substantially as herein described with reference to the examples.

DATED this 4th day of NOVEMBER, 1991

SOCIETE DES PRODUITS NESTLE S.A.

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