



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A23P 1/12, A23K 1/16, 1/18	A1	(11) International Publication Number: WO 95/16367 (43) International Publication Date: 22 June 1995 (22.06.95)
(21) International Application Number: PCT/US94/14027 (22) International Filing Date: 13 December 1994 (13.12.94) (30) Priority Data: 08/168,016 15 December 1993 (15.12.93) US (71) Applicant (for all designated States except US): THE QUAKER OATS COMPANY [US/US]; Suite 25-7, 321 N. Clark Street, Chicago, IL 60610 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): LEE, Patrick, S. [US/US]; 26 East Cunningham Drive, Palatine, IL 60067 (US). LOUIS, Camille, A. [US/US]; Apartment F, 2310 West Nichols Road, Arlington Heights, IL 60004 (US). (74) Agents: JOHNSON, Lars, S. et al.; Suite 25-7, 321 N. Clark Street, Chicago, IL 60610 (US).		(81) Designated States: AM, AT, AU (Petty patent), BB, BG, BR, BY, CA, CH, CN, CZ, DE, DE (Utility model), DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PROCESS FOR PREPARING RETORT-STABLE, SHAPED FOOD PIECES (57) Abstract The present invention relates to a process for preparing a cohesive, retort-stable, shaped food piece, said process comprising: (a) preparing a premixture comprising (1) from about 20 % to about 80 % by weight gluten, (2) from about 20 % to about 80 % by weight flour, (3) from 0 % to about 50 % by weight meat and bone meal, (4) from 0 % to about 9 % by weight fat, (5) from 0 % to about 0.7 % by weight added sulfur, (6) from 0 % to about 2 % by weight dicalcium phosphate, wherein the weight percentage of the premixture components are expressed as a percentage of the premixture; (b) combining the premixture with water to form a secondary mixture, wherein the ratio of premixture to water is in the range of from about 1.6:1 to about 4:1; (c) mixing the secondary mixture for a period of time sufficient to obtain a substantially uniformly mixed dough and under conditions such that the temperature of the secondary mixture and uniformly mixed dough in the mixing operation are maintained in the range of from about 15 °C to about 45 °C; and (d) forming the uniformly mixed dough into a desired shaped piece, wherein the forming operation is carried out in conjunction with low specific mechanical energy and high pressure conditions, and under conditions such that the temperature of the uniformly mixed dough in the forming operation is in the range of from about 40 °C to about 100 °C, and wherein said shaped piece is cohesive and maintains its shape when retorted. The present invention further relates to a piece prepared by the above-described process.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

PROCESS FOR PREPARING RETORT-STABLE, SHAPED FOOD PIECES

5

10

FIELD OF INVENTION

The present invention relates to a process for preparing a retort-stable, shaped food piece which is cohesive and maintains its shape when retorted. The present invention further relates to the retort-stable, shaped food piece prepared by the process of the present invention.

15

BACKGROUND OF INVENTION

Pet owners typically have a great deal of affection for their pets. Many, in fact, consider their pets to be members of their families, and treat them accordingly by indulging them to a great degree. One of the ways owners indulge their pets is by the food they purchase for them. In this context, many owners derive pleasure from feeding their pets foods which contain shaped food pieces which the owner identifies with the particular type of pet. An example of this would be a bone-shaped food piece in a dog food.

20

25

Of course, these shaped food pieces must also contribute to satisfying the nutritional requirements for the particular pet. To accomplish this, the shaped pieces are preferably prepared from proteinaceous and farinaceous material. The term proteinaceous material refers to glutens such as wheat gluten. Proteinaceous material obtained from other sources such as defatted oil seed protein material; and other known proteinaceous sources (e.g., meat, fish, etc.) are not of use

30

in the present invention. The term farinaceous material refers to cereal flours such as wheat flour.

One problem in preparing such shaped pieces is that many pet foods have to undergo the extreme processing conditions of a retort sterilization procedure. For certain shaped proteinaceous materials, such as meat analogs, this is not a concern. These meat analogs retain their analog properties even when subjected to a retort operation. However, these meat analogs are structurally different than the shaped pieces of the present invention in that they are typically prepared from texturized vegetable protein (TVP) and may have a striated texture. By "striated texture" it is meant that the shaped piece tends to have a texture analogous to muscle striations. This striated texture allows the shaped piece to be easily torn apart along the striations, and as such the piece does not have to maintain a distinct and definite shape when subjected to a retort operation.

The shaped pieces of the present invention do not have such a striated texture, however, but instead are, for the most part, cohesive. Until now, shaped pieces having a cohesive texture like those of the present invention could not withstand the extreme conditions of a retort operation, but would typically dissolve when retorted. This would be undesirable since the shaped piece would not maintain its original shape and form, but would be unrecognizable.

Thus, shaped food pieces having the cohesive consistency of the shaped pieces of the present invention are useful only when they are retort-stable, i.e., do not dissolve upon

hydration and/or retorting, but maintain their desired shape. The present invention provides such a piece, as well as a process for its preparation.

BACKGROUND ART

5 There are numerous processes known in the art for producing shaped, extruded, edible proteinaceous products.

 U.S. Patent 3,968,268, issued July 6, 1976 to Sair et al., discloses a process for producing hydratable, translucent to glassy, proteinaceous products, and the resulting products themselves. In the claimed process a water-moistened, edible
10 proteinaceous material having at least about 40% by weight protein, on a dry weight basis, and an effective amount of water, within the range of about 10 to 50%, is subjected to working under effective mechanical pressure with added heat
15 sufficient to convert it to a hot, moist, plastic extrudable mass. This hot, plastic mass is extruded through and from a length of a temperature controlled, elongated die under non-puffing conditions. The extruded product is unpuffed, substantially homogeneous, translucent to glassy, and
20 characterized by having texture and retaining its structural integrity under retorting conditions. This product is alleged to be pleasing in the mouth and have protein cell bodies with the pleasing feel, firmness, structure, texture, coarseness, or bite characteristics found in uncooked or cooked food
25 products.

 Sair et al. also teach that in their process the proteinaceous material must be heated to a sufficiently high temperature to retain retort stability. Specifically, they

teach that extruded proteinaceous materials which are extruded at temperatures of 180°F., 210°F., and 230°F., completely disintegrate when subjected to retorting. This is contrary to what has been found in the present invention, where the products are shaped and formed at low dough temperatures and maintain their shape when retorted.

U.S. Patent 3,965,268, issued June 22, 1976 to Stocker et al., refers to an expanded protein product comprising a sulfur-containing organic compound. Stocker et al. claim a method of preparing an expanded edible protein product having an open, cellular structure, the method comprising forming an admixture of proteinaceous material having a protein content of at least about 30% by weight, from about 0.05% to about 2.0% by weight of said proteinaceous material of a sulfur-containing organic compound selected from the group consisting of cysteine hydrochloride, D,L-methionine, sodium lignosulfonate, thiamine mononitrate, calcium thioglycollate, and mixtures thereof, and water in an amount sufficient to result in a moisture content of 15% to about 50% by weight of said admixture; heating the mix to a temperature above about 220°F; mechanically working the heated mix at a pressure substantially above atmospheric pressure; and expanding the mix by suddenly releasing the pressure. The expanded product has a crisp, crunchy texture which lends itself to use in a large number of foodstuffs, for example snack items.

As can be seen, the product of the process taught by Stocker et al. has a different texture than the shaped edible piece of the present invention. Furthermore, the process

taught by Stocker et al. includes a heating step which is not required in the process of the present invention.

As already stated herein, it is also known to make a striated, texturized shaped meat analog. This technology uses
5 a vegetable protein, or extract, along with a sulfur-containing compound, typically a sulfur-containing amino acid or pure sulfur itself, to make the striated, texturized piece. An extrusion process operated under high shear and temperature conditions is typically used to manufacture this meat analog.
10 The high shear and temperature conditions facilitate the cross-linking of the vegetable proteins.

The resulting extruded meat analog is typically very porous, and upon hydration expands to several times its dry weight and size. The hydrated meat analog is also porous and
15 is spongy to the touch and chew. After retorting, the hydrated and retorted meat analog is spongy and soft. The meat analog is easily torn apart following retorting, due to its striated structure.

As can be seen, there is nothing in the art which teaches
20 the shaped piece prepared by the process of the present invention. It is therefore an object of the present invention to provide a process for preparing such a shaped food piece which is cohesive and maintains a definite and distinct shape and integrity when hydrated and/or retorted.

25 It is another object of the present invention to provide an edible, shaped food piece which is cohesive and maintains a definite and distinct shape and integrity when hydrated and/or retorted.

These objects are accomplished by the invention described herein.

Unless otherwise specified, the weight percentages provided herein for the components of the premixture are on a
5 wet basis.

SUMMARY OF THE INVENTION

The present invention relates to a process for preparing a cohesive, retort-stable, shaped food piece, said process comprising:

- 10 (a) preparing a premixture comprising
 - (1) from about 20% to about 80% by weight gluten,
 - (2) from about 20% to about 80% by weight flour,
 - (3) from 0% to about 50% by weight meat and bone meal,
 - 15 (4) from 0% to about 9% by weight fat,
 - (5) from 0% to about 0.7% by weight added sulfur,
 - (6) from 0% to about 2% by weight dicalcium phosphate, wherein the weight percentage of the premixture components are expressed as a
20 percentage of the premixture;
- (b) combining the premixture with water to form a secondary mixture, wherein the ratio of premixture to water is in the range of from about 1.6:1 to about 4:1;
- 25 (c) mixing the secondary mixture for a period of time sufficient to obtain a substantially uniformly mixed dough and under conditions such that the temperature of the secondary mixture and uniformly mixed dough

in the mixing operation are maintained in the range of from about 15°C to about 45°C; and

- (d) forming the uniformly mixed dough into a desired shaped piece, wherein the forming operation is carried out in conjunction with low specific mechanical energy and high pressure conditions, and under conditions such that the temperature of the uniformly mixed dough in the forming operation is in the range of from about 40°C to about 100°C, and wherein said shaped piece is cohesive and maintains its shape when retorted.

The present invention further relates to a piece prepared by the above-described process.

DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises a process for preparing a retort-stable, shaped food piece. The piece maintains its shape when hydrated and retorted, e.g., if the piece is originally formed in a bone shape, the hydrated piece will maintain the bone shape and the retorted piece will maintain the bone shape.

In the process of the present invention a premixture is initially prepared. The premixture comprises from about 20% to about 80%, preferably from 20% to about 40%, more preferably from about 25% to about 35% by weight gluten; from 0% to about 50%, preferably from about 1% to about 30%, more preferably from 2% to about 15% by weight meat and bone meal; from about 20% to about 80%, preferably from about 30% to about 75%, more preferably from about 35% to about 65% by

weight flour; from 0% to about 9%, preferably from about 1% to about 8%, more preferably from about 3% to about 6% by weight fat; from 0% to about 0.7%, preferably from about 0.01% to about 0.5%, more preferably from about 0.1% to about 0.2% by weight added sulfur; and from 0% to about 2%, preferably from about 0.1% to about 1% by weight dicalcium phosphate.

The gluten of the present invention is preferably wheat gluten. It is believed that other glutens, such as corn gluten, may work in the present invention as well. These other glutens may also be combined with wheat gluten in the premixture.

Wheat gluten is a concentrated natural protein in the form of a light tan powder having a bland taste and aroma. Wheat gluten is known to consist mainly of gliadin (prolamine) and glutenin (glutelin), which are the principle cereal proteins, together with other components of the endosperm cell. Wheat gluten is separated from wheat flour by a washing method known to those skilled in the art.

The precise amount of gluten contained in the premixture of the present invention, while within the range of from about 20% to about 80% by weight, is dependent upon the particular type of gluten being utilized. The preferred wheat gluten comprises from about 20% to about 80%, preferably from about 20% to about 40%, more preferably from about 25% to about 35% by weight of the premixture. The gluten may be provided to the premixture in the form of isolated gluten added to the premixture, gluten inherent in the flour present in the premixture, and mixtures thereof.

The flour used in the present invention can be any type of flour obtained from known grains. Examples of flours useful in the present invention include, but are not limited to, wheat flour, corn flour, oat flour, and mixtures thereof, with wheat flour being preferred.

As with the gluten, the precise amount of flour used in preparing the premixture of the present invention, while within the range of from about 20% to about 80% by weight, is dependent upon the particular type of flour being utilized. For example, when wheat flour is used the premixture comprises from about 20% to about 80%, preferably from about 30% to about 70%, more preferably from about 50% to about 65% by weight wheat flour; when corn flour is used the premixture comprises from about 35% to about 70%, preferably from about 35% to about 60%, more preferably from about 35% to about 50% by weight corn flour.

Other types of cereal flours known to those skilled in the art can be used in the present invention. The precise amounts of these cereal flours useful herein will fall within the range of from about 20% to about 80% by weight, and can be determined by one skilled in the art.

The fat which may be added to the premixture of the present invention may be obtained from any fat source known to those skilled in the art. Examples of fat sources useful in the present invention include, but are not limited to, choice white grease, beef tallow, soy oil, corn oil, vegetable oil, and mixtures thereof, with choice white grease being the preferred fat source.

The amount of a particular fat source that must be used in the premixture is that amount necessary to provide a total fat content in the premixture in the range of from 0% to about 9%, preferably from about 1% to about 8%, more preferably from about 3% to about 6% by weight. Of course, the required amount of a particular fat source necessary to achieve this will vary for differing fat sources. However, this is something one skilled in the art can determine. When the preferred choice white grease is used as the fat source, the premixture comprises from 0% to about 9%, preferably from about 1% to about 8%, more preferably from about 3% to about 6% by weight choice white grease.

When fat is included in the premixture of the present invention it facilitates the process of the present invention by lubricating the material flow through the forming operation, thereby lowering shear and energy transfer to the product.

The sulfur which may be added to the premixture of the present invention may be in the form of pure sulfur or either as an organic or inorganic sulfur-containing compound.

This sulfur is considered "added sulfur" and is added to the premixture separately from the other premixture ingredients and in a manner sufficient to contribute the specified amount of sulfur to the premixture. Sulfur may also be present in the other premixture ingredients (e.g., gluten, flour, etc.), but any such amounts are typically not significant and are not considered when determining the amount of sulfur added to the premixture.

Any type of sulfur-containing compound useful in the preparation of edible foodstuffs may be used in preparing the premixture of the present invention. Examples of useful sulfur-containing organic compounds include, but are not limited to, sulfur-containing amino acids, lower alkyl mercaptans, lower alkyl sulfides, lower alkyl disulfides, thioacids, and other compounds, for example thiamine, may be employed. Among these, compounds such as cysteine, cystine, methionine, thiodipropionic acid, thioglycollin, thiamine, lignosulfonic acid, and their salts are preferred, with methionine being most preferred.

The amount of a particular sulfur source that must be used in the premixture is that amount sufficient to provide a total added sulfur content in the premixture in the range of from 0% to about 0.7%, preferably from about 0.01% to about 0.5%, more preferably from about 0.1% to about 0.2% by weight of the premixture. Of course, the required amount of a particular sulfur source necessary to achieve this will vary for differing sulfur sources, although falling within the broad range specified above, and will be appreciated by one skilled in the art. When the preferred methionine is used as the sulfur source, it comprises from 0% to about 2%, preferably from about 0.1% to about 1%, more preferably from 0.2% to 0.5% by weight of the premixture.

The dicalcium phosphate, when added to the premixture of the present invention, comprises from 0% to about 2%, preferably from about 0.1% to about 1% by weight of the premixture.

The meat and bone meal, when added to the premixture of the present invention, is a source of protein and flavor. When used, the meat and bone comprises from 0% to about 50%, preferably from about 1% to about 30%, more preferably from about 2% to about 15% by weight of the premixture. There is no known preferred source of meat and bone meal, and as such the meat and bone meal can be obtained from any commercial source known to one skilled in the art.

Other optional ingredients which may be added to the premixture of the present invention include, but are not limited to, edible fiber sources, nutritional supplements, soy grits, coloring agents, and flavoring agents.

When such optional ingredients are added to the premixture, the levels at which they are added will vary depending upon the particular optional ingredient. When soy grits are included in the premixture they typically comprise from 0% to about 30%, preferably from 1% to about 15%, more preferably from about 2% to about 7% by weight of the premixture.

When adding the meat and bone meal, fat, sulfur, dicalcium phosphate, and other optional ingredients, care must be taken to avoid adding amounts of such ingredients which may disrupt the formation of a gluten matrix. If such disruption occurs, then retort stability may be adversely affected.

Coloring agents and flavoring agents are added to the premixture at levels necessary to impart the desired flavor and color to the final product, which will be dependent upon the preferences of the particular formulator. Such coloring

and flavoring agents are typically added to the premixture at levels of less than 1% by weight.

The premixture is next combined with water to form a secondary mixture. The ratio of the premixture to water is in the range of about 1.6:1 to about 4:1, preferably from about 1.65:1 to about 2.5:1, more preferably from about 1.65:1 to about 1.85:1.

Any type of water may be used to form the secondary mixture of the present invention, i.e., deionized water, purified water, distilled water, tap water, etc. Of course, care should be taken to ensure that the water does not contain any impurities that may have an adverse effect on the final shaped piece produced in the present invention, i.e., particulate matter that might interrupt the gluten structure and adversely affect retort stability.

After the secondary mixture is prepared, it is mixed for a period of time sufficient to obtain a substantially uniformly mixed dough. Care must be taken to avoid mixing the secondary mixture past the point of minimum mobility or the dough (gluten structure) breaks down, and the resulting piece will not be retort stable. The minimum mobility of the secondary mixture can be determined by one skilled in the art.

The secondary mixture may be mixed by any method and/or apparatus known to those skilled in the art. Examples of mixing methods and/or apparatus useful in the present invention include, but are not limited to, a paddle mixer, a ribbon mixer, and a Hobart mixer (auger mixer), with a ribbon mixer being preferred.

The secondary mixture is mixed under conditions such that its temperature and the temperature of the resulting uniformly mixed dough are maintained in the range of from about 15°C to about 45°C, preferably from about 20°C to about 30°C, more preferably from about 20°C to about 25°C.

The length of time necessary for mixing the secondary mixture to obtain the substantially uniformly mixed dough will depend upon the method of mixing used. When a ribbon mixer is used, the secondary mixture is typically mixed for a period of time in the range of from about 2 to about 10 minutes, preferably from about 3 to about 8 minutes, more preferably from about 4 to about 6 minutes.

After the substantially uniformly mixed dough is prepared, it is formed into the desired shaped piece. It is important that this forming operation or step take place in conjunction with low specific mechanical energy and under high pressure conditions. The low specific mechanical energy and high pressure conditions act in combination to provide the structural bonding necessary to have a retort-stable, final shaped piece.

The forming operation is carried out in conjunction with specific mechanical energy in the range of from about 6 watt·hr./kg. to about 70 watt·hr./kg., preferably from about 6 watt·hr./kg. to about 50 watt·hr./kg., more preferably from about 6 watt·hr./kg. to about 35 watt·hr./kg., and under a pressure of at least about 400 psig, preferably at least about 500 psig, more preferably at least about 600 psig. If the pressure under which the forming takes place is too low, a

final cohesive shaped piece will not be produced, but instead discrete separate individual particles will result from the forming operation. Furthermore, even if the pressure is sufficient to provide a uniform, solid, discrete, shaped piece, it still must be high enough to allow for some expansion of the uniformly mixed dough after the forming pressure is released. By this it is meant that there must be sufficient pressure in the forming operation that when the pressure is released, the shaped dough product will have a slight expansion due to release of the pressure alone. The expansion is not due to any gas evolved after the pressure release or any other internal forces, other than the plastic reformation of the shaped product material.

It is also important that the forming operation take place under conditions such that the temperature of the uniformly mixed dough remains in the range of from about 40°C to about 100°C, preferably from about 40°C to about 90°C, more preferably from about 45°C to about 90°C, still more preferably from about 60°C to about 80°C. The specific mechanical energy and pressure will contribute to the increase in temperature of the substantially uniformly mixed dough as it is being formed into the desired shaped piece. However, care should be taken to minimize the temperature rise during the forming of the dough in order to minimize gelatinization of the dough and keep the dough temperatures within the ranges specified herein.

Although gelatinization of the starch is minimized, some gelatinization is necessary to form the desired shaped piece.

However, if there is too much gelatinization the formed piece becomes highly hydrophilic and is not retort stable. The correct degree of gelatinization will provide a product which is neutral to hydrophobic. It is also possible that an overly
5 gelatinized piece will form an expanded cell structure, which can cause the shaped piece to lack retort integrity as well.

The temperature of the substantially uniformly mixed dough is also kept low to avoid generating steam during the forming operation and causing the piece to have an expanded
10 cell structure. If any steam is generated, then when the pressure is released during the forming operation it is possible that the steam will expand the shaped piece, causing the shaped piece to have an undesirable texture and lack retort integrity. All of these problems can be avoided by
15 maintaining the temperature of the dough below its gelatinization point.

In a preferred embodiment of the present invention, the forming operation takes place in a low shear extruder. The low shear extruder in essence is an extruder which operates
20 under low specific mechanical energy conditions and produces a product having a low dough temperature. Cooling of the low shear extruder maybe necessary to control the dough temperature if the specific mechanical energy causes the temperature to rise too high. However, this is unlikely under
25 the low specific mechanical energy conditions under which the forming operation is carried out.

In this preferred embodiment, the low shear extruder is operated at a speed in a range of from about 40 to 60 RPM,

preferably from about 45 to about 60 RPM, more preferably from about 50 to about 60 RPM; the temperature of the dough as it exits the low shear extruder is in the range of from about 40°C to about 85°C, preferably from about 45°C to about 65°C, more preferably from about 50°C to about 60°C; the pressure at the exit of the low shear extruder is at least about 400 psig, preferably at least about 500 psig, more preferably at least 600 psig; and the dough is extruded at a rate of 100 to 300 kg. dough per hr., preferably from about 100 to about 275 kg. dough per hr., more preferably from about 100 to about 250 kg. dough per hr.

In the present invention it has been found that a 4" diameter Bonnot 5-zone extruder is a preferred low shear extruder. While the reason for this preference is not exactly known, it is believed that the Bonnot extruder has a particularly desirable screw profile for use in the process of the present invention. This extruder is available from The Bonnot Company, located in Uniontown, Ohio.

Another way of forming the uniformly mixed dough into the desired shaped piece is to charge the uniformly mixed dough into a cylinder having a die head and a punch mechanism. When the cylinder is used, the punch mechanism is pressed into the dough-containing cylinder to cause the dough to be extruded through the die head, thereby forming the dough into an extruded rope having the desired cross-sectional shape. This extruded rope is then cut cross-sectionally along its length to obtain a discrete piece having the desired shape.

While not intending to be bound by theory, it is

surprising and unexpected that the gluten and flour, and especially wheat gluten and wheat flour, when processed under the low specific mechanical energy, low dough temperature, and high pressure conditions of the process of the present invention produces a cohesive shaped piece which maintains its distinctive definitive shape upon hydration and retort. This is especially unexpected when it is considered that the product of the present invention is prepared using a low specific mechanical energy, low temperature, high pressure forming process. As already stated herein, the prior art teaches that high temperature extrusion (i.e., forming) is necessary to obtain a retort-stable piece. The art teaches that temperatures of at least about 250°F are necessary for preparing a retort-stable product, and that retorted, proteinaceous extruded products which are extruded at temperatures of 180°F, 210°F, and 230°F dissolve when retorted.

A preferred process of the present invention comprises:

- (a) preparing a premixture comprising
- (1) from about 25% to about 35% by weight wheat gluten,
 - (2) from about 50% to about 65% by weight wheat flour,
 - (3) from 2% to about 15% by weight meat and bone meal,
 - (4) from 3% to about 6% by weight choice white grease,
 - (5) from 0.2% to about 0.5% by weight methionine,

- (6) from 0.1% to about 1% by weight dicalcium phosphate;
- (b) combining the premixture with water to form a secondary mixture, wherein the ratio of premixture to water is in the range of from about 1.65:1 to about 1.85:1;
- (c) mixing the secondary mixture in a ribbon mixer for a period of time in the range of from about 4 to about 6 minutes, thereby obtaining a substantially uniformly mixed dough, wherein said mixing is carried out under conditions such that the temperature of the secondary mixture and uniformly mixed dough in the mixing operation are maintained in the range of from about 20°C to about 25°C; and
- (d) forming the uniformly mixed dough into a desired shaped piece in a low shear extruder, wherein extruder is operated at a speed in the range of from about 50 to 60 RPM, the dough exit temperature is in the range of from about 50°C to about 60°C, the exit pressure is at least 600 psig, and the specific mechanical energy provided by the extruder is in the range of from about 6 watt·hr./kg. to about 35 watt·hr./kg.

The present invention also relates to a cohesive, retort-stable, shaped food piece prepared by the method comprising:

- (a) preparing a premixture comprising
- (1) from about 20% to about 80% by weight gluten,
 - (2) from about 20% to about 80% by weight flour,

- (3) from 0% to about 50% by weight meat and bone meal,
- (4) from 0% to about 9% by weight fat,
- (5) from 0% to about 0.7% by weight added sulfur,
- 5 (6) from 0% to about 2% by weight dicalcium phosphate, wherein the weight percentage of the premixture components are expressed as a percentage of the premixture;
- (b) combining the premixture with water to form a
- 10 secondary mixture, wherein the ratio of premixture to water is in the range of from about 1.6:1 to about 4:1;
- (c) mixing the secondary mixture for a period of time sufficient to obtain a substantially uniformly mixed
- 15 dough and under conditions such that the temperature of the secondary mixture and uniformly mixed dough in the mixing operation are maintained in the range of from about 15°C to about 45°C; and
- (d) forming the uniformly mixed dough into a desired
- 20 shaped piece, wherein the forming operation is carried out in conjunction with low specific mechanical energy and high pressure conditions, and under conditions such that the temperature of the uniformly mixed dough in the forming operation is in
- 25 the range of from about 40°C to about 100°C, and wherein said shaped piece is cohesive and maintains its shape when retorted.

The present invention is further illustrated, but not

limited by, the following examples.

EXAMPLES

Example 1

5 A premixture containing 25 lb. wheat gluten, 65 lb. wheat flour, 6 lb. choice white grease, 2 lb. of methionine, 2 lb. dicalcium phosphate, and 0.5 lb. of titanium dioxide is initially prepared and blended for 2 minutes in a Buffalo Mixer (which is a ribbon blender). Water is added to this
10 blended premixture at a weight ratio of 2:1 (blended premixture:water) to prepare a wet mixture. The wet mixture is blended in the Buffalo Mixer for another 10 minutes to form a dough.

 The dough is removed from the mixer fed to a 4 inch
15 diameter, 5 zone Bonnot extruder using a "Bonnot #5" (designated by Bonnot) screw shaft. The exit of the extruder is fitted with a die having a single opening capable of making a product in the shape of a bone.

 The extruder is operated at 60 RPM (screw rotation speed)
20 and the body of the barrels is jacketed with cold water in the first two zones (numerating the zones starting from the feed inlet to the exit of the extruder) with nothing jacketing the last 3 zones. The dough is fed into the extruder at a rate as fast as the rotating screw can convey it away from the feed
25 inlet (this is known as "choke-fed").

 After operating for about 5 minutes the process reaches a state of equilibrium. The dough is being fed at about 200 kg./hr. The exit temperature of the product is 170°F (62°C)

and the pressure, as measured at an outlet immediately before the die-assembly, is approximately 600 psig.

As the extrudate emerges from the die it is cut in pieces having a thickness of approximately 1/8 to 3/8 inch. The cut
5 pieces are conveyed away from the pelletizer by a cool air stream which facilitates transfer and prevents the cut pieces from adhering to each other. The collected cut pieces are dried in a Proctor and Schwartz dryer for 2 hours until their overall moisture content is less than 12% w/w basis.

10 The dried cut pieces are placed in cans of pet food along with other components, such as meat pieces and gravy. The amount of cut pieces in each can is 3% and the gravy (which is essentially 95% water) comprises 50 wt. % of the can contents. The overall moisture content of the canned ingredients is
15 approximately 80%. The cans are sealed and retorted at 250°F for 65 minutes. The resulting retorted canned contents include the "bone-shaped" extruded pieces. The bone shape of the extruded pieces is essentially the same shape as the opening in the die. The "bone-piece" can be handled without
20 losing its integrity.

Example 2

A dry mixture consisting of 283 lb. wheat gluten, 318 lb. meat and bone meal, 353 lb. wheat flour, 60 lb. choice white grease, 21 lb. methionine, 21 lb. dicalcium phosphate, and 4
25 lb. of titanium dioxide is blended for 2 minutes in a Buffalo Mixer (which is a ribbon blender). To 250 lb. of this mixture, 125 lb. of water is added. The "wet mixture" is then blended in the Buffalo Mixer for another 10 minutes.

The wet mixture ("the dough") is now removed from the mixer and ready to be fed to the extruder. The extruder used is a 4 inch diameter 5 zone Bonnot extruder using a "Bonnot #5" (designated by Bonnot) screw shaft. The exit of the extruder is fitted with a die consisting of a single rectangular opening (a "slit" shape) with the dimension of 1/8 inch width by 5/8" inch length.

The extruder is operating at 40 RPM (screw rotation speed) and the body of the barrels is jacketed with cold water in the first two zones (numerating the zones starting from the feed inlet to the exit of the extruder) and saturated steam at 15 psig jacketing the last 3 zones. The dough is fed into the extruder at a rate as fast as the rotating screw can convey it away from the feed inlet (this is also known as "choke-fed").

After operating for about 5 minutes at a rotating speed of 40 RPM and dough fed in continuously, the entire process has reached a state of equilibrium. The dough is being fed at about 300 kg./hr. The exit temperature of the product is 180°F (68°C) and the pressure, as measured at an outlet immediately before the die-assembly, is approximately 390 psig.

As the extrudate emerges from the die, it is pelletized by an attached multi-knife cutter. The cutting speed is set sufficiently fast to produce cut pieces of thickness of approximately 1/2 to 1 inch long, resulting in rectangular pieces. The kibble thus produced is then conveyed away from the pelletizer by a cool stream of air to facilitate transfer and to prevent the kibbles from adhering to each other. The

collected kibbles are then dried in a Proctor and Schwartz dryer for 2 hours until the kibbles has reached an overall moisture of 8% w/w basis.

5 The dry kibble is now put into cans of pet foods along with other components, such as meat pieces and gravy. The amount of kibbles in each can is 3% and the gravy (which is essentially 95% water) is 50%; the overall moisture of the can content is 80%. The cans are sealed and retorted at 250°F for 65 minutes. The resulting canned contents include "flat-
10 shaped" extruded pieces. The cross sectional shape of the extruded pieces is essentially the same shape as the opening in the die. The "flat-piece" can be handled without losing its integrity.

Example 3

15 A dry mixture consisting of 190 lb. wheat gluten, 118 lb. wheat flour, 20 lb. choice white grease, 7 lb. dicalcium phosphate, 2 lb. of titanium dioxide, and 1 lb. of a aluminum lake color (yellow #6), is blended for 2 minutes in a Buffalo Mixer (which is a ribbon blender). To 250 lb. of this
20 mixture, 125 lb. of water is added. The "wet mixture" is then blended in the Buffalo Mixer for another 10 minutes.

The wet mixture ("the dough") is now removed from the mixer and ready to be fed to the extruder. The extruder used is a 4 inch diameter 5 zone Bonnot extruder using a "Bonnot
25 #5" (designated by Bonnot) screw shaft. The exit of the extruder is fitted with a die consisting of 9 circular openings and each opening has a diameter of 1/8 inch.

The extruder is operating at 57 RPM (screw rotation

speed) and the body of the barrels is jacketed with cold water jacketing all 5 zones. The dough is fed into the extruder at a rate as fast as the rotating screw can convey it away from the feed inlet (this is also known as "choke-fed").

5 After operating for about 5 minutes at a rotating speed of 57 RPM and dough fed in continuously, the entire process has reached a state of equilibrium. The dough is being fed at about 250 kg./hr. The exit temperature of the product is 155°F (54°C) and the pressure, as measured at an outlet
10 immediately before the die-assembly, is approximately 800 psig.

As the extrudate emerges from the die, it is pelletized by an attached multi-knife cutter. The cutting speed is set sufficiently fast to produce cut pieces of thickness of
15 approximately 1 to 1 1/2 inch long. The "strand" kibble thus produced is then conveyed away from the pelletizer by a cool stream of air to facilitate transfer and to prevent the kibbles from adhering to each other. The collected kibbles are then dried in a Proctor and Schwartz dryer for 2 hours
20 until the kibbles has reached an overall moisture of 10% w/w basis.

The dry kibble is now put into cans of pet foods along with other components, such as meat pieces and gravy. The amount of kibbles in each can is 3% and the gravy (which is
25 essentially 95% water) is 50%; the overall moisture of the can content is 80%. The cans are sealed and retorted at 250°F for 65 minutes. The resulting canned contents include "strand-shaped" extruded pieces. The shape of the extruded pieces is

essentially circular in diameter and slightly longer than the original extruded piece. The "strand-piece" can be handled without losing its integrity.

Example 4

5 A premixture containing 97 lb. wheat gluten meal, 128.25 lb. wheat feed flour, 4.75 lb. methionine, and 4.75 lb. dicalcium phosphate is initially hand dumped and blended in a ribbon mixer for 3 minutes. To the initial mixture, 14.25 lb. choice white grease is added and blended for 5 minutes to form
10 the blended premixture. Water is added to the blended premixture at a weight ratio of 2.37:1 (blended premixture:water) to prepare a wet mixture. The wet mixture is blended in the ribbon mixer for an additional 5 minutes to develop a uniform dough.

15 The dough is manually removed from the mixer and manually fed to a 4" diameter, 5-zone Bonnot extruder using a Bonnot #5 screw (the extruder is fitted with a 15 HP motor). The exit of the extruder is fitted with a die insert with a single opening capable of making a definitively shaped product (e.g.,
20 bone, fish, wedge). For optimum conditions, the extruder is operated empty for at least 10 minutes prior to the introduction of the wet dough. This operating time serves as a warm-up and facilitates achieving steady-state conditions within five minutes of manufacturing.

25 The extruder is operated at 59 RPM (screw rotation speed) and the body of the barrel is jacketed with cold water in the first two zones (the numbering starts with the feed inlet and ends at the exit of the extruder). The third and fifth zones

of the extruder are left at ambient conditions and the fourth zone is steam jacketed. The dough is choke-fed into the extruder. By "choke-fed" it is meant that there is more material in the extruder hopper than the screw can convey
5 through the barrel instantly.

Within five minutes the process achieves steady state conditions. The dough is fed at about 225 kg./hr and exits the extruder at a temperature between 65-70°C under a pressure between 400-600 psig. Both the temperature and pressure are
10 measured immediately before the extruder outlet.

As the extrudate exits the die assembly, it is face-cut to form pieces having a thickness of approximately 1/8 to 3/8 inch. The cut pieces are conveyed via an air-cooled conveyor with a wire mesh belt. The cool air reduces stickiness due to
15 evaporative flashing. The air-cooled pieces are collected in wire mesh trays and dried in a Proctor & Schwartz batch oven for 2.5 hours at 93°C or until the moisture content is less than 10% on a wet basis. The product is dried for stability during storage but can be used in a canned product without the
20 preliminary drying.

The dried, shaped pieces are included as a component in canned dog food with other dog food components, including meat and gravy. The shaped, extruded piece is included as 3% of the final can weight, including gravy. The ratio of gravy to
25 component is generally about 48:52 (gravy:components). The canned components and gravy are sealed and retorted for 65 minutes at 120°C. The final product includes the retort-stable shaped pieces in a chunk and gravy matrix. The shaped

pieces, upon hydration, weigh about 3 times their original weight and have increased in size by at least 25%. By "retort stable" it is meant that the shaped piece can be easily handled without changing shape, breaking apart, or losing the identity of the original shape.

5

CLAIMS

1. A process for preparing a cohesive, retort-stable, shaped food piece, said process comprising:
- 5 (a) preparing a premixture comprising
- (1) from about 20% to about 80% by weight gluten,
 - (2) from about 20% to about 80% by weight flour,
 - (3) from 0% to about 50% by weight meat and bone meal,
 - 10 (4) from 0% to about 9% by weight fat,
 - (5) from 0% to about 0.7% by weight added sulfur,
 - (6) from 0% to about 2% by weight dicalcium phosphate, wherein the weight percentage of the premixture components are expressed as a
 - 15 percentage of the premixture;
- (b) combining the premixture with water to form a secondary mixture, wherein the ratio of premixture to water is in the range of from about 1.6:1 to about 4:1;
- 20 (c) mixing the secondary mixture for a period of time sufficient to obtain a substantially uniformly mixed dough and under conditions such that the temperature of the secondary mixture and uniformly mixed dough in the mixing operation are maintained in the range
- 25 of from about 15°C to about 45°C; and
- (d) forming the uniformly mixed dough into a desired shaped piece, wherein the forming operation is carried out in conjunction with low specific

mechanical energy and high pressure conditions, and under conditions such that the temperature of the uniformly mixed dough in the forming operation is in the range of from about 40°C to about 100°C, and
5 wherein said shaped piece is cohesive and maintains its shape when retorted.

2. A process according to claim 1 wherein the premixture comprises from about 20% to about 40% by weight wheat gluten,
10 from about 30% to about 70% by weight wheat flour, from about 1% to about 30% meat and bone meal, from about 1% to about 8% by weight choice white grease, from about 0.1% to about 1% by weight methionine, and from about 0.1% to about 1% dicalcium phosphate.

15

3. A process according to claim 2 wherein the ratio of premixture to water is in the range of from about 1.65:1 to about 2.5:1.

20 4. A process according to claim 3 wherein the secondary mixture is mixed in a paddle mixer for a period of time in the range of from about 3 minutes to about 8 minutes.

5. A process according to claim 4 wherein the uniformly
25 mixed dough is formed into the desired shaped piece in a low shear extruder.

6. A process according to claim 5 wherein the extruder is

operated at a pressure of at least about 500 psig.

7. A process according to claim 6 wherein the specific mechanical energy of the extruder is in the range of from about 6 watt·hr./kg. to about 50 watt·hr./kg., wherein the extruder is operated at a speed in the range of from about 45 to about 60 RPM, and wherein the temperature of the dough exiting the forming extruder is in the range of from about 45°C to about 90°C.

10

8. A process for preparing a cohesive, retort-stable, shaped food piece, said process comprising:

(a) preparing a premixture comprising

15

(1) from about 25% to about 35% by weight wheat gluten,

(2) from about 50% to about 65% by weight wheat flour,

(3) from about 2% to about 15% by weight meat and bone meal,

20

(4) from about 3% to about 6% by weight choice white grease,

(5) from about 0.2% to about 0.5% by weight methionine,

(6) from about 0.1% to about 1% by weight dicalcium phosphate;

25

(b) combining the premixture with water to form a secondary mixture, wherein the ratio of premixture to water is in the range of from about 1.65:1 to

about 1.85:1;

- 5 (c) mixing the secondary mixture in a ribbon mixer for a period of time in the range of from about 4 to about 6 minutes, thereby obtaining a substantially uniformly mixed dough, wherein said mixing is carried out under conditions such that the temperature of the secondary mixture and uniformly mixed dough in the mixing operation are maintained in the range of from about 20°C to about 25°C; and
- 10 (d) forming the uniformly mixed dough into a desired shaped piece in a low shear extruder, wherein the extruder is operated at a speed in the range of from about 50 to 60 RPM, the dough exit temperature is in the range of from about 50°C to about 60°C, the exit
- 15 pressure is at least 600 psig, and the specific mechanical energy provided by the extruder is in the range of from about 6 watt·hr./kg. to about 35 watt·hr./kg.

20 9. A cohesive, retort-stable, shaped food piece prepared by the process comprising:

- (a) preparing a premixture comprising
- (1) from about 20% to about 80% by weight gluten,
- (2) from about 20% to about 80% by weight flour,
- 25 (3) from 0% to about 50% by weight meat and bone meal,
- (4) from 0% to about 9% by weight fat,
- (5) from 0% to about 0.7% by weight added sulfur,

- (6) from 0% to about 2% by weight dicalcium phosphate, wherein the weight percentage of the premixture components are expressed as a percentage of the premixture;
- 5 (b) combining the premixture with water to form a secondary mixture, wherein the ratio of premixture to water is in the range of from about 1.6:1 to about 4:1;
- (c) mixing the secondary mixture for a period of time
10 sufficient to obtain a substantially uniformly mixed dough and under conditions such that the temperature of the secondary mixture and uniformly mixed dough in the mixing operation are maintained in the range of from about 15°C to about 45°C;
- 15 (d) forming the uniformly mixed dough into a desired shaped piece, wherein the forming operation is carried out in conjunction with low specific mechanical energy and high pressure conditions, and under conditions such that the temperature of the
20 uniformly mixed dough in the forming operation is in the range of from about 40°C to about 100°C, and wherein said shaped piece is cohesive and maintains its shape when retorted.
- 25 10. A cohesive, retort-stable, shaped food piece prepared by the method comprising:
- (a) preparing a premixture comprising
- (1) from about 25% to about 35% by weight wheat

gluten,

(2) from about 50% to about 65% by weight wheat flour,

(3) from about 2% to about 15% by weight meat and bone meal,

(4) from about 3% to about 6% by weight choice white grease,

(5) from about 0.2% to about 0.5% by weight methionine,

(6) from about 0.1% to about 1% by weight dicalcium phosphate;

(b) combining the premixture with water to form a secondary mixture, wherein the ratio of premixture to water is in the range of from about 1.65:1 to about 1.85:1;

(c) mixing the secondary mixture in a ribbon mixer for a period of time in the range of from about 4 to about 6 minutes, thereby obtaining a substantially uniformly mixed dough, wherein said mixing is carried out under conditions such that the temperature of the secondary mixture and uniformly mixed dough in the mixing operation are maintained in the range of from about 20°C to about 25°C; and

(d) forming the uniformly mixed dough into a desired shaped piece in a low shear extruder, wherein the extruder is operated at a speed in the range of from about 50 to 60 RPM, the dough exit temperature is in the range of from about 50°C to about 60°C, the exit

pressure is at least 600 psig, and the specific mechanical energy provided by the extruder is in the range of from about 6 watt·hr./kg. to about 35 watt·hr./kg.

INTERNATIONAL SEARCH REPORT

Int. onal Application No

PCT/US 94/14027

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A23P1/12 A23K1/16 A23K1/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A23P A23K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,3 968 268 (LOUIS SAIR ET AL.) 6 July 1976 cited in the application see column 2, line 60 - line 64 see column 4, line 39 - column 5, line 23 see column 13, line 22 - line 26 see column 13, line 52 - column 14, line 34 see claims 1-22 --- -/--	1,9

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

27 April 1995

Date of mailing of the international search report

17. 05. 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+ 31-70) 340-3016

Authorized officer

Dekeirel, M

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 94/14027

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,4 015 026 (MORRIS P. BURKWALL ET AL.) 29 March 1977 see column 3, line 32 - line 54 see column 4, line 3 - line 40 see column 4, line 66 - column 5, line 13 see column 5, line 58 - line 61 see column 6, line 21 - line 50 see column 7, line 32 - line 51 see examples 1-3,6,7 see claims 1-4,6,7 ---	1,9
Y	GB,A,1 433 976 (THE QUAKER OATS COMPANY) 28 April 1976 see page 2, line 41 - line 65 see page 3, line 44 - line 70 see page 3, line 90 - line 98 see example 1 ---	1,9
A	EP,A,0 071 331 (RALSTON PURINA COMPANY) 9 February 1983 see example 1 see claims 1-10 ---	1,9
A	US,A,3 965 268 (CHARLES T. STOCKER ET AL.) 22 June 1976 cited in the application see the whole document ---	1-10
A	US,A,4 419 372 (C. LAWRENCE GREENE ET AL.) 6 December 1983 see column 4, line 53 - column 5, line 22 see claims 1,7 ---	1
A	US,A,4 524 081 (ARUN K. BANSAL) 18 June 1985 see column 4, line 61 - column 5, line 14 see claims 1-3 ---	1
A	JOURNAL OF FOOD SCIENCE, vol.57, no.6, 1992, CHICAGO US pages 1282 - 1284 N. UNKLESBAY ET AL. 'Thermophysical properties of extruded beef/corn flour blends' see page 1283; table 1 -----	1

INTERNATIONAL SEARCH REPORT

information on patent family members

Int: onal Application No

PCT/US 94/14027

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3968268	06-07-76	AU-A- 5939073 CA-A- 1019620 DE-A- 2343830 GB-A- 1439983 US-A- 3978244 US-A- 3978236	20-02-75 25-10-77 14-03-74 16-06-76 31-08-76 31-08-76
US-A-4015026	29-03-77	CA-A- 1067747	11-12-79
GB-A-1433976	28-04-76	BE-A- 824217 CA-A- 1035994 FR-A- 2274235 LU-A- 71622 NL-A- 7500230 SE-A- 7500285	09-07-75 08-08-78 09-01-76 09-12-75 16-12-75 15-12-75
EP-A-0071331	09-02-83	CA-A- 1189741 JP-C- 1670757 JP-B- 3032343 JP-A- 58023751 CA-A- 1189740 JP-C- 1670758 JP-B- 3032344 JP-A- 58023752	02-07-85 12-06-92 10-05-91 12-02-83 02-07-85 12-06-92 10-05-91 12-02-83
US-A-3965268	22-06-76	NONE	
US-A-4419372	06-12-83	NONE	
US-A-4524081	18-06-85	US-A- 4542686	24-09-85