

**COMPOSITION FOR PREPARATION OF SEAFOOD PRESERVE,
PREPARATION PROCESS AND PRESERVE SO OBTAINED**

5 The present invention relates to a composition adapted for the preparation of canned seafood. It also relates to a process for the preparation of the said canned seafood and to the canned seafood thus obtained.

10 By the expression "canned seafood" or "preserved seafood", there is denoted within the meaning of the invention every packaging of foodstuffs, especially of seafood, within hermetically closed packagings, the said products being prepared by way of a sterilization treatment at high temperature during a short period, the said treatment being intended to eliminate any
15 microorganism comprising spores, which microorganisms are proper to reproduce themselves under non-refrigerated storage and distribution conditions.

20 The seafood which is contemplated within the meaning of the invention is consisting of seafood such as mussels, shellfish such as shrimp or crab and more generally fish of any nature.

 The industry of seafood cannery and more especially of shellfish cannery is subjected to very severe requirements.

25 As a matter of fact, the final consumer requires that the canned product presents a texture which is considered from the point of view of firmness under the teeth and from the point of view of touch, as close as possible to that of the product just having been fished.
30 The said consumer also requires that the said product presents a natural colour, a non altered taste and more generally that it keeps the whole of its organoleptic qualities.

35 Now, these requirements were hardly consistent with - on the one hand, the fact that between the moment at which the said seafood is fished and the moment at which

it is canned, there may elapse a more or less long duration during which the products can be subjected to various modifications which are undesirable and,

5 - on the other hand, the fact that once they reach the place where they are canned, they are subjected to treatments which may damage one or several of the essential qualities hereabove recalled.

10 In that connection, before reaching the cannery, the seafood may undergo alterations of their texture under the action of endogeneous enzymes and/or of contaminating bacteria, which bacteria may also generate a denaturation of the constituting parts of the said products. Shellfish, in particular, under the action of the time, undergo undesirable chemical transformations which become apparent
15 by modifications of the colour, the oxidation of certain constituents of their meat leading, for example, to a darkening of the colour.

20 Within the cannery, the sterilization treatment at high temperature, while eliminating the contaminating microorganisms which may be present, produces also sometimes as a result a loss of texture, especially of firmness.

25 The whole of the research work which has been carried out until today to improve the quality of canned seafood and to satisfy the consumer, has consequently been essentially directed to an improvement of the texture, of the colour and of the taste.

30 In order to improve the texture, it has above all been proposed to add salt to the product and to wash in a second step with water the salted products in order to eliminate a part of this salt; nevertheless, salt remains present at concentrations which are relatively high, the said concentrations producing an especially unpleasant taste and having bad consequences for the health. As a
35 matter of fact, salt is known to be a factor which favours high blood pressure which is due to the fact that the

sodium is retained. Furthermore, repeated washings produce as a result aroma losses which are detrimental with respect to the organoleptic qualities of the finally obtained products.

5 As far as the undesirable changes in colour are concerned, it was noticed that they are above all the result of chemical transformations of the constituents of the meat of the seafood.

10 These chemical transformations are especially the source of the formation of blue pigments in the products concerned. In that case, the metalloenzymes, in other words the tyrosinases and the phenoloxidases which are naturally present in shellfish meat, oxidize in the presence of copper and of iron the hydroxyl groups of the phenols which are also a part of the constitution of the
15 meat. Once oxidized, the said phenols condense with one another and provide compounds of high molecular weight, i.e. melamines, whose colour varies from blue to black according to the degree of oxidization of the medium.

20 On the other hand, the proteinic components of the seafood contain sulphured elements which, during the sterilization, transform into sulphured hydrogen which reacts with the ferrous ions of the metal of the cans and provide iron sulphide which is black.

25 Solutions have already been proposed to prevent the formation of these colorations. For example, in order to prevent the formation of iron sulphide, it is well known to use cans whose inner surface is varnished or enamelled; it is also known to interpose between the meat and the
30 walls of the can a parchment paper, possibly impregnated by a solution of zinc salt. Besides the fact that these measures increase the cost of the canned seafood, they did not provide really satisfactory results.

35 From a more general standpoint of view, in order to prevent the formation as well of the melamines as of the iron sulphide, it has been proposed to incorporate a

foodgrade acid, for instance citric and/or acetic acid, into the seafood in order to diminish on the one hand the pH to acid values and on the other hand to complex the metallic ions Fe^{++} , Cu^{++} , Mg^{++} , which participate to the chemical transformations which lead to the formation of the coloured compounds; the acids in question are generally associated with salt which is proper to preserve the texture of the products.

The incorporation of the said acids did not provide a complete satisfaction. The reason is that the thus obtained products have a very pronounced acid taste which is absolutely unpleasant and which is added with the taste of the excess of salt; the organoleptic qualities of the products are degraded while the contents in coloured compounds are not significantly decreased.

The chemical transformations undergone by the meat of the seafood can also lead to the formation of crystals of struvite or of ammonium and magnesium phosphate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$); these crystals are the result of an association during the preparation of the canned food, between PO_4^{3-} groups and the magnesium which are present within the meat and the NH_4^+ groups produced by the degradation of the proteins. The crystallization occurs when the products are cold and continues during storage.

These crystals while non toxic, are absolutely undesirable because of the unpleasant sensation which occurs when the product is consumed.

In order to prevent the formation of the said crystals, it was proposed to use the type of solution already proposed in order to prevent colouring.

Other compositions have also been proposed to stabilize the qualities of texture, of colour and of taste of the canned seafood: these compositions comprise different types of sequestering agents whose role is to lock the metallic ions implicated in the reactions of formation of colourings and of crystals of struvite.

In that connection, it has been proposed to use additional compositions on the basis of phosphates and of citrates (Japanese Patent Application No. JP 51-41465), or on the basis of phosphates and of ethylenediamine tetra-acetic acid or EDTA ("Handbook of Food Additives", 2nd edition, 1972, pages 737-738). The canned seafood treated with the said compositions remain relatively unstable during storage. It oxidizes and still presents dark coloration. Furthermore, the crystals of struvite are not totally eliminated; finally, the organoleptic properties of the thus obtained products are improvable.

On the other hand, as well EDTA as the phosphates are not considered as safe from the medical and from the ecological standpoint of view.

Consequently, other solutions were proposed to avoid the use of that type of products.

In that connection, the European Patent Application EP-A-O 190 028 proposes to use gluconodeltalactone or GDL as additive in canned seafood.

GDL provides relatively good results as far as the taste of the fresh product is concerned with respect to the product obtained when the canned food is additioned with salt and citric acid. On the contrary, the results obtained from the standpoint of view of texture of the product and of the colouring phenomenons as well as of the formation of crystals of struvite, are not totally satisfactory in contradiction with which is mentioned in the said patent application.

Furthermore and in different fields,

- american patent US-A-3 745 027 proposes the use of polyhydric alcohols and antimycotic agents such as sorbic, propionic and benzoic acids in processes for the dehydration of foodstuffs comprising meat, vegetables or fruit,
- japanese patent JP 60-130377 (Derwent abstract 8534) discloses the use of seasonings selected from among

sodium glutamate, sorbitol, phosphoric acid and gluconodeltalactone for the preparation of cod roe intended to be packed in a plastic film envelope,

- 5 - patent application EP-A-0 012 255 discloses the use of moistening agents such as polyols, foodgrade acids such as citric acid and acidulants such as gluconodeltalactone or acid sodium pyrophosphate for intermediate moisture foodstuffs subjected to a mild pasteurization treatment.

10 Consequently, an object of the present invention is above all to overcome the drawbacks of the prior art by proposing a composition adapted to the preparation of canned seafood, the said composition providing the said products, once canned, with improved properties as well
15 from the standpoint of view of texture as from the standpoint of view of colouring.

Applicants have had the merit to find that said object is reached when using for the preparation of the canned seafood a composition which comprises an efficient
20 amount of, on the one hand, at least one acidogenic agent and/or of at least one of its derivatives and, on the other hand, of at least one sugar-alcohol.

Consequently, the composition according to the invention, adapted to the preparation of canned seafood,
25 is characterized by the fact that it comprises at least one acidogenic agent and/or at least one of its derivatives as well as at least one sugar-alcohol.

The expression "acidogenic agent" denotes every substance neutral from the point of view of the pH and adapted, after solubilization in aqueous medium, of hydro-
30 lyzing progressively with formation of an acid. That substance is selected from the group comprising gluconolactones, glucoheptonolactones and their equivalents and/or their mixtures, preferably gluconolactones and, still more preferably, gluconodeltalactone or GDL.
35

Among the derivatives of the acidogenic agent

adapted to be used within the composition according to the invention, salts such as gluconates and gluconoheptonates may be mentioned.

5 The expression "sugar-alcohol" denotes every hydrogenated derivative of saccharidic compounds, especially sorbitol, mannitol, xylitol; sorbitol is preferred.

10 According to an advantageous embodiment of the composition according to the invention, the latter comprises from 1 to 75% by weight of acidogenic agent and from 25 to 99% by weight of sugar-alcohol; preferably, the composition comprises from 6.5 to 33% by weight of GDL and from 67 to 93.5% by weight of sorbitol.

15 According to another advantageous embodiment of the composition according to the invention, the latter comprises GDL and sorbitol.

20 The combination GDL-sorbitol is especially efficient. Applicants assume, without wishing to be bound by that hypothesis, that the said results are obtained due to the favourable effect of the sorbitol on the well-known sequestering power of GDL.

25 Furthermore, sorbitol has an influence from the osmotic point of view and authorises probably a shifting of the equilibrium in water within the canned product in favour of the canning juice which contains the composition according to the invention. Due to that fact, the tendency of the products to absorb the said juice is limited, fact which is absolutely favourable from the point of view of firmness.

30 Furthermore, sorbitol presents a sweetening power of only 0.7, i.e. equal to 0.7 times the sweetening power of sucrose. It is consequently possible to incorporate into the composition relatively important amounts of sorbitol without causing a modification of the sweet taste within the products sufficiently important to be detected.

35 Traditionally, the canned seafood are prepared along the following steps:

- extracting the meat of seafood intended to be canned,
- subjecting the said meat to a bleaching treatment according to which the said meat is contacted with a bleaching juice at a high temperature, during a duration
5 sufficient to stabilize it, the said bleaching treatment being followed by a dripping step and by a washing step with water,
- canning the thus treated meat with a canning juice and hermetically closure of the can,
- 10 - subjecting the thus closed can to a sterilization treatment.

Applicants have found that the above-identified composition according to the invention can also be used at the moment of the bleaching treatment.

15 Consequently, the process according to the invention is characterized by the fact that, at the moment of the canning step, an efficient amount of the composition according to the invention is used.

20 The expression "efficient quantity" denotes a quantity below which the drawbacks of the prior art are not overcome, especially as far as the firmness of the products is concerned.

Advantageously, the composition according to the invention can be used as a constituent of the bleaching juice.
25

According to an advantageous embodiment of the process according to the invention, a composition according to the invention is used as well during the bleaching step as during the canning step.

30 According to another advantageous embodiment of the process according to the invention, the pH of the canning juice is adjusted at a value comprised between 6 and 7, preferably between about 6 and 6.5, either by means of the composition according to the invention when the latter
35 comprises an acidogenic agent, or by way of a foodgrade acid when the said composition comprises a derivative of

an acidogenic agent.

The foodgrade acid can be selected from the group comprising citric, acetic, hydrochloric, tartric and lactic acids.

5 When it is used within the bleaching juice, the composition according to the invention is used, with respect to the total weight of the bleaching juice, in an amount such that the said bleaching juice comprises from 0.2 to 3% by weight, preferably from 0.7 to 1.5% by weight
10 of acidogenic agent, especially of GDL and from 1 to 15% by weight, preferably from 3 to 10% by weight of sugar-alcohol, especially of sorbitol.

The bleaching juice can also comprise salt, especially sodium chloride, and an antioxidant, for instance
15 sodium metabisulfite. In that case, the salt content of the bleaching juice is preferably lower than 3% by weight, and the concentration in antioxidant is comprised generally between 0.1 and 0.2% by weight.

In order to carry out the bleaching step using the composition according to the invention, the seafood meat
20 is dipped within the bleaching juice comprising the said composition and then the temperature is raised until about 100°C and maintained at that value during 10 to 15 minutes, preferably during about 12 minutes, after which
25 the bleached meat is washed with water.

Surprisingly, it was noticed that the bleaching juice comprising the composition according to the invention is particularly little aggressive with respect to the seafood meats: it preserves their colour, their texture
30 and especially their firmness to the touch and does not provide any toxicity.

When used within the canning juice, the composition according to the invention is used in an amount such that the canning juice comprises from 0.2 to 2% by weight,
35 preferably from 0.7 to 1.1% by weight of acidogenic agent, especially of GDL and from 1 to 12% by weight, prefe-

rably from 4 to 10% by weight of sugar-alcohol, especially of sorbitol.

5 The canning juice can also contain salt, especially sodium chloride representing from 1 to 4% by weight of the total weight of the canning juice, preferably about 2.5%. At this concentration, the salt has no negative influence on the finally obtained products from the organoleptic point of view.

10 Of course, the amounts of GDL and of sorbitol used as well in the canning juice as in the bleaching juice may vary as a function of the nature of the products within the above-mentioned concentrations limits.

That selection is a routine operation for those skilled in the art of canned seafood.

15 The sterilization treatment to which the bleached and canned meat is subjected, is well-known by itself (see for example "L'industrie alimentaire halieutique" by Marcel SAINCLIVIER ISSN 03708411 - 1988). In any case, the sterilization conditions vary as a function of the nature and of the size of the seafood considered as well as of the size of the cans.

20 For example, the "conditions" of sterilization within cylindrical containers whose dimensions are 86 x 44.5 mm, are as far as crabs are concerned, from 30 to 50 minutes, preferably about 40 minutes at a temperature comprised between 100 and 130°C, preferably about 115°C while, in the case of shrimps, it is from 15 to 35 minutes, preferably about 25 minutes at a temperature comprised between 100 and 130°C, preferably about 115°C.

25 The invention also concerns the canned seafood consisting of hermetically closed and sterilized containers and characterized by the fact that the canning juice comprises an efficient quantity of the composition according to the invention.

30 The invention will be well understood with the help of the following description of an advantageous embodiment

of the invention and by way of comparative examples, with respect to the canning of shrimps, illustrated by the following drawing in which:

- 5 - figure 1 is a graphical representation of the variation of luminance expressed in % as a dependent variable of time T expressed in weeks at a temperature of 40°C,
- 10 - figure 2 is a graphical representation of the variation of the firmness F expressed in Newtons as a dependent variable of time T expressed in weeks at a temperature of 40°C.

15 In the hereafter described examples concerning the canning of shrimps, the said shrimps are prepared according to the traditional method which comprises the steps of washing, shelling and selection.

 Then, the shrimps are bleached. In that connection, they are dipped in the bleaching juice in a proportion of 80 by weight of shrimps for 100 by volume of bleaching juice.

20 The bleaching is carried out at 100°C during 12 minutes.

 After having been drained off, the shrimps are washed three times with cold water.

25 They are then canned, covered with the canning juice and sterilized at 115°C during 25 minutes.

30 In order to study the behaviour of the shrimps during storage, the cans are stoved at a temperature of 40°C. Thus, the speeds of the oxidation reactions are increased (speed multiplied by two times when the temperature is increased by 10°C: law of Arrhenius of the first order or degree). Thus, one week at 40°C corresponds to about 4 weeks at 20°C.

35 The firmness and the coloration of the thus prepared shrimps, stocked during 8 weeks at 40°C, were determined using the following determination methods:

a) - Method for the determination of the brightness or

luminance

The luminance is evaluated with the help of a chromometer, for instance the chromometer marketed under the trademark CR-200 by Minolta. The sample is illuminated with the help of a lamp and only the light which is reflected perpendicularly with respect to the surface is recovered by the optical fiber for the analysis of the luminance.

By way of the knowledge of the luminance, it is possible to appreciate the degree of coloration of the product as the oxidation of the fish meat results in a dark colour. The more "L" is low, the more the product is oxidized. On the contrary, the more "L" is high, the less the product is oxidized, and consequently the better is the quality of the sample.

In order to set a uniform sample, the latter is finely crushed. A Petri box is filled with the crushed material. The measurements are carried out on different points of the box. For each experience, two samples are prepared. The indicated value corresponds to the average value of ten measurements.

b) - Method for the determination of the firmness

The firmness of the shrimps has been evaluated with the help of an INSTRON 4500 device comprising a 100 N cell and a rectangular stamp or punch (19 x 40 mm). The test has been carried under an assigned deformation at a compression speed of 10 mm/min.

The results are expressed in Newtons (average of 5 measurements).

The shrimps measured are selected in such a way that shrimps having approximately the same size (thickness: 6 to 7 mm; weight: 0.32 to 0.38 g) are obtained. Thus, the differences observed on the measurements are not due to the sample, but to the treatment to which the sample during its preparation has been subjected.

EXAMPLE

Preparation of canned shrimps with the help of different bleaching and canning juices.

The compositions of the juices are indicated in the following Table I.

5 The formulations 1 and 3 correspond to the prior art formulations while the formulation 2 corresponds to the invention.

 The indicated amounts represent percentages by weight with respect to the total weight of the juices.

10

TABLE I

	Components	Formulation 1	Formulation 2	Formulation 3
5 Bleaching juice	GDL	0	0.4	0.6
	EDTA	0.02	0	0
	Phosphates	0.1	0	0
	Citric acid	0.08	0	0
	Na metabisulfite	0.16	0.16	0.16
	Salt	1	1	1
	Sorbitol	0	4	0
	Water	qsp 100	qsp 100	qsp 100
10 Canning juice	GDL	0	0.4	0.6
	EDTA	0.02	0	0
	Phosphates	0.4	0	0
	Citric acid	0.1	0	0
	Salt	2.5	2.5	2.5
	Sugar	2.2	0	0
	Sorbitol	0	7	0
	Water	qsp 100	qsp 100	qsp 100

15 As above indicated, the cans are stocked during 8 weeks at a temperature of 40°C, then their firmness and their luminance are evaluated as indicated hereabove.

20 The results of the measurements of the variation of the luminance are shown on Figure 1 and are represented by two curves C₁ and C₂ which respectively correspond to the products 1 and 2.

25 It is noticed that the luminance L is higher for the shrimps prepared using formulation 2 according to the invention. The oxidation phenomenons are consequently less pronounced as in the case of formulation 1.

 When using in the juices used for the preparation of the canned seafood, a composition according to the invention, there is obtained a stabilization of the luminance which is higher than the stabilization noticed with

a formulation according to the prior art.

The firmness results are illustrated by Figure 2 which shows three lines, respectively D_1 , D_2 and D_3 , representing the variation of the firmness of products 1, 2 and 3 as a dependent variable of time.

It is noticed that, when using formulation 2 according to the invention, the firmness of the shrimps is improved with respect to the formulations according to the prior art 1 and 3.

C L A I M S

1. Composition adapted for the preparation of
canned seafood, characterized by the fact that it comprises
from 1 to 75% by weight of at least one acidogenic
agent selected from the group comprising gluconolactones,
glucoheptonolactones and their equivalents and/or their
mixtures, especially gluconolactones, and/or at least one
of the derivatives of the said acidogenic agent as well as
from 25 to 99% by weight of at least one sugar-alcohol
selected from the hydrogenated derivatives of saccharidic
compounds and especially from the group comprising sorbitol,
mannitol, xylitol.

2. Composition according to claim 1, characterized
by the fact that it comprises from 6.5 to 33% by weight of
gluconodeltalactone and from 67 to 93.5% of sorbitol.

3. Process for the preparation of canned seafood
in which:

- the meat of a seafood intended to be canned is
extracted,
- the said meat is subjected to a treatment or
bleaching step according to which the said meat is
contacted with a bleaching juice at a high
temperature, during a duration sufficient to
stabilize it, then the said meat is dripped and
washed with water,
- the said meat is canned with a canning juice
during a canning step, then the can is
hermetically closed,
- the thus closed can is subjected to a
sterilization treatment at a temperature comprised
between 100 and 130°C,

characterized by the fact that an efficient amount of a
composition according to one of claims 1 and 2 is used at
the moment of the canning step.

4. Process for the preparation of canned seafood
in which:



- the meat of a seafood intended to be canned is extracted,
 - the said meat is subjected to a treatment or bleaching step according to which the said meat is contacted with a bleaching juice at a high temperature, during a duration sufficient to stabilize it, then the said meat is dripped and washed with water,
 - the said meat is canned with a canning juice during a canning step, then the can is hermetically closed,
 - the thus closed can is subjected to a sterilization treatment at a temperature comprised between 100 and 130°C,
- characterized by the fact that an efficient amount of a composition according to one of claims 1 and 2 is used at the moment of the bleaching step.

5. Process according to claim 3, characterized by the fact that, in order to carry out the canning step, there is used an amount of the composition according to one of claims 1 and 2 such that the canning juice comprises from 0.2 to 2% by weight, preferably from 0.7 to 1.1% by weight, of acidogenic agent, especially of gluconodeltalactone and from 1 to 12%, preferably from 4 to 10% by weight, of sugar-alcohol, especially of sorbitol.

6. Process according to claim 4, characterized by the fact that, in order to carry out the bleaching step, there is used an amount of the composition according to one of claims 1 and 2 such that the canning juice comprises from 0.2 to 3% by weight, preferably from 0.7 to 1.5% by weight, of acidogenic agent, especially of gluconodeltalactone and from 1 to 15%, preferably from 3 to 10% by weight, of sugar-alcohol, especially of sorbitol.

7. Process according to one of claims 3 to 6, characterized by the fact that the pH of the canning juice is fixed at a value comprised between 6 and 7, preferably



between 6 and 6.5, either with the help of the composition according to the invention when the latter contains an acidogenic agent, or with the help of a foodgrade acid when the said composition comprises a derivative of an

5 acidogenic agent.