

## **Appendix 5 A proposal to increase the value of farmed seaweed in Kaledupa, SE Sulawesi, Indonesia**

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### **Summary**

This report shows that training and the development of a carrageenan processing plant on Kaledupa would have the potential to double the annual income for 600 fishers who also have sea weed farms in the Kaledupa area. Participation in the scheme would be tied to surrender of fishing licences so that it provides an alternative income for those coming out of the fishery. This proposal could provide the mechanism to enable the Kaledupa reef fishery to recover so Maximum Sustainable Yields could be achieved for the remaining fishers rather than the current significantly depressed catch rates. The initial investment to establish this business is in the region of £200,000 (note this is a rough estimate only based on UK prices). It is proposed therefore that if after consideration of this proposal, the logic of the scheme is accepted by the Trustees that additional funding from the Darwin Initiative budget is targeted at producing a detailed specification and costing for the business. This would then be forwarded to funding bodies such as COREMAP. Successful implementation of a project such as this could have significant benefits for other sea weed growing communities in eastern Indonesia to provide substantially greater benefits from their sea weed production.

### **Introduction**

I was asked by Operation Wallacea Trust as part of the Darwin Initiative (Project Ref. No: 162/16/002 'Building capacity for sustainable fisheries management in the Wallacea region') to undertake the following:

1. To identify the potential markets in the UK and Europe amongst the pharmaceutical industry and other outlets for agar and carrageen products.
2. To identify on site the sea weed species currently being cultured, the drying techniques being utilised and the prices obtained by the farmers for these products. To develop proposals for improving the drying techniques to enhance the quality of the final product.

By way of background information, it was understood that there was some difficulty experienced by Kaledupan seaweed farmers in producing high-quality 'agar' and that this may be due to their drying techniques. As a result, their 'agar' had a low gelling value (due to its low molecular weight) and a consequential low price. As will be shown, this has been found probably not to be the case. However, a second strand was the need to increase the value of the crop so as to reduce these farmers' reliance on fishing the coral reefs. This contributes to the current over-fishing problem in the ecologically valuable and environmentally sensitive Wakatobi Marine National Park.

Accordingly, a visit to Hoga and Kaledupa took place in July/August 2007. Opwall kindly provided supporting facilities such as accommodation and, most importantly, the services of an interpreter, Wawan Kidner. To them and to him my grateful thanks.

## **Potential Markets**

It is necessary to distinguish between the seaweed products 'agar' and 'carrageenan'.

Agar is derived from tropical species such as *Gracilaria* and *Gelidium* and is primarily used as a bacterial culture media by medical and biological research establishments worldwide. Although it may be farmed, much is gathered by beach collectors. It is a relatively small, stable but significant market. In 1990 world production was about 7,000 MT /annum (MT = Metric ton) of product <sup>(1)</sup>. There was no evidence of agar farming during my visit. However, in the Indo-Pacific, it is a commonplace term for any farmed seaweed.

Carrageenan, is derived from the two closely related tropical eucheumatoid seaweeds *Kappaphycus alvarezii* and *Eucheuma denticulatum*. Virtually all production is from farmed sources. The farming originated in the Philippines in the 1960's and from there has steadily expanded to all tropical marine countries, though the Philippines and now Indonesia are the major producers. In Kaledupa, *Kappaphycus alvarezii* is the dominant species being grown,

In 1990 world production was about 67,000 MT/annum of dried seaweed of which about 50,000 MT was from the Philippines and 14,500 MT from Indonesia <sup>(1)</sup>.

By 2001 world production had risen to 110,000 MT/annum and in 2005 expanded to 150,000-200,000 MT/annum, resulting in an estimated 100m USD/annum farmgate income to many tens of thousands of farmers <sup>(2)</sup>.

By 2007 the estimated production in Indonesia is matching the Philippines at about 85,000 MT/annum each. However, the significant difference between these two countries is that in the Philippines about 86% of the dried crop has undergone value-added processing whereas in Indonesia the figure is nearer 23% <sup>(2)</sup>.

What is driving this continued rise in production? It is the combination of ease and simplicity of seaweed culture and the great utility of carrageenan in many processed food and other industries – see Appendix 3. New uses for carrageenan are continually being discovered which increase demand. Perhaps most importantly the rapid rise in affluence of emerging countries like China, India and Brazil, with their huge populations, will ensure demand continues as they seek to achieve Western levels of lifestyle <sup>(3)</sup>.

Until the mid 90's carrageenan was always manufactured by a capital-expensive and energy-intensive process of extraction and purification. This involved either, using solvents like the alcohol series, or by freeze-thaw and pressing techniques, to produce a 'Refined Carrageenan' product. Because carrageenan rapidly becomes too thick to pump or otherwise handle at quite low concentrations then the size of the plant, and its water requirement, also had to be excessively large. Nevertheless, many major corporations invested heavily in Europe, the USA and the Indo-Pacific to establish processing plants.

Much to the concern of these corporations, certain companies in the Philippines, such as the Shemberg Corporation, discovered an alternative process, which though still shrouded in excessive secrecy, produced a far cheaper carrageenan product. Instead of boiling the seaweed to extract a viscous carrageenan which then required purification by

the above-mentioned methods, the principle was to leave the carrageenan in-situ in the cellulose matrix of the original plant material and simply extract impurities from it whilst simultaneously improving its gelling properties.

This new carrageenan could be used in almost all the situations where refined carrageenan had previously been dominant, at about half the price. The only significant sector where it could not be used is in clear drinks, since, because of its cellulose content, it is opaque.

These major corporations vigorously lobbied governments at the time to prevent the use of this new category of product, variously called Processed Eucheuma Seaweed (PES) Philippines Natural Grade (PNG) or Semi Refined Carrageenan (SRC) or Seaweed Flour (SF). Only the first two, PES/PNG could be used for human consumption. The latter two, SRC/SF, were even cheaper but, due to higher bacterial load, are only suitable for pet-food or industrial purposes. As with the term agar, all four of the above terminologies are now becoming intermixed. This can lead to confusion unless care is taken.

Despite the intensive negative lobbying in the late 1990's and early 2000's PES/PNG became internationally accepted for food use and in Europe is designated as E407a. Full details of worldwide purity standards can be found in Appendix 2. Ironically, these same major corporations, realising that they need to live in the real world, are now buying or establishing plants to make PES or are buying-in the product to make specialized mixtures or grades of carrageenan adapted to the varied food processing requirements that exist.

From the above, it can be considered that PES is a world-wide commodity, though not in the sense of having an established trading floor where it can be bought and sold. It is always traded in US dollars (\$) or USD). Current (October 2007) quotations for food-grade PES FOB and in metric ton quantities were obtained from two Philippine and two Chinese sources and are as follows:

1. China \$4,230 - \$4,830/MT (according to powder size)
2. China \$4,500/MT
3. Philippines \$4,950/MT
4. Philippines \$4,150 - \$5,200/MT (according to grade)

It is usually the buyer's preference to pay freight and quotations vary from \$200 - \$600/MT into Southampton. Occasionally buyers may prefer a CIF price.

*Note:*

*FOB is 'Free On Board'. It is the price offered on condition that the seller meets all costs until the goods are loaded on the ship at the port of export. The buyer meets all further costs.*

*CIF is 'Cost, Insurance and Freight'. It means that the selling price includes the cost of the goods, all the freight or transport costs (including loading/unloading) and the cost of marine insurance.*

When averaged, the typical price for PES is about \$4,650/MT or \$4.65/Kg. At current exchange rates (October 2007) this equates to about 42,400 Indonesian rupiahs (IDR)/Kg.

It is important to note that the current price for dried seaweed received by Kaledupan farmers is about 4,000IDR - 4,500 IDR/Kg i.e. ten times less (Source - Pak Beloro, chief of local Forkani).

### **Enhancing the Quality and Value**

During my visit I examined fresh and dried *Kappaphycus alvarezii* seaweed grown at two widely separated sites – Buranga, Kaledupa and Darawa, Lintea. This included snorkelling to look at the seaweed in situ.

The visual look of the fresh seaweed was excellent. Apart from very occasional and limited evidence of tip-nibbling by (probably) Rabbitfish and Parrotfish, the overall crop would have scored highly in the crop condition index formulated by SEAPlantNet<sup>(4)</sup>. Discussion with Pak Sava Ali, a seaweed farmer in Buranga, suggested that farmers growing in shallower water may experience greater problems with tip-nibbling. Another farmer, Pak Jumani from Darawa, agreed that more nibbling was associated with shallows but thought the weed compensated for nibbling by growing thicker stems, and there was generally no loss of production as a result. It is useful to note that Jumani is also a buyer and has contacts with the major local buyers. He was trained by Pak Suryadi (employed by Marcel Trading Corporation - a major Philippine producer and by the local WWF).

This tells us little about either the quantity or quality of the carrageenan within the crop but must act as an optimistic indicator of both. Sava Ali thinks the local variety is 'flower' type. Jumani said that Marcel Trading Corporation (based in the Philippines) introduced a new variety, locally called 'Kunusum', three years ago and this much improved production. This suggests that the Kaledupan farmers are probably growing the up-to-date higher yielding varieties.

The issue of drying the crop was raised both with Sava Ali and at a village meeting of farmers in Darawa which I attended. Sava Ali suggested no problems, even in the monsoon season. However some concern was expressed by the Darawa farmers as to when a crop is considered sufficiently dry, which is normally 35% moisture or less. The carrageenan content significantly degrades as the moisture level rises to 40% in insufficiently dried material. On the other hand, overdried material, especially below 25% moisture, whilst good from a quality point of view, is too stiff and brittle to compress well during bailing for export<sup>(5)</sup>.

A simple solution would be to organise a training session, using a moisture meter to show these farmers the 'feel' and look of the crop at different levels of dryness and when adequately dry. Perhaps the moisture meter might then be donated to the general seaweed-farming community for their continued use?

It was noticed that the 'strings' on which the seaweed is grown were spaced surprisingly far apart – between one or even two metres. Elsewhere, it is suggested that line spacings of as little as 0.2m can be used, according to conditions<sup>(4)</sup>. When questioned, both farmers said they preferred the wider spacing to improve access by boat and to prevent inter-tangling of the strings. In Darawa farmers choose one metre but in Langge 2-3 metres is preferred. Jumani tried half-metre separation but said it reduced production. Received wisdom suggests that only when self-shading of the crop occurs would production be affected so it is hard to understand why such wide spacings are

chosen. If it is a genuine biological phenomenon that is occurring then it requires further investigation. If not, it may be that a cultural/convenience motive is in play.

The outcome of such wide spacings is that overall production is probably well below optimum <sup>(6)</sup>. Sava Ali gave figures for his farm that result in a production value of 600Kg/month of dry crop. Beloro gave an overall figure for the Kaledupa area that was yet lower at 400Kg/month/farm. This compares with 800Kg - 2,500Kg/month/farm elsewhere in the region <sup>(7)</sup>. This is a significant discrepancy, which, if correct, suggests much higher overall production for this area is possible, within the same seabed area currently taken by farming. To this can be added possible expansion to new areas – in 2000 a figure of 30% additional increase was suggested <sup>(8)</sup>. It is not known to what extent this 'slack' of unused seabed has been filled in the interim.

One strategy for additional income would be to discover, by additional research (sociological as well as technical), the precise reason for the generous line spacings. A training program should then take place to persuade and convince the farmers that tighter spacings will give a directly proportionate greater additional income. If need-be, some should be taken to other locations where this already occurs, to give them tangible proof. The target and outcome should be at least a doubling of production per farm to 800 Kg dry seaweed per month, which, in itself, is only at the bottom of the range of production elsewhere.

Beloro provided me with an estimate of 1,200 farmers within the Kaledupa area. There are an estimated 1,345 fishers in this same area, so this figure for number of seaweed farmers appears credible<sup>(9)</sup>. There need not be precise parity between the two figures, since not all farmers are fishermen nor all fishermen farmers. Given the earlier figure of each farm producing 400Kg/month, this gives an estimated total production value of dried seaweed for the area of 5,760MT/annum.

Using the previously quoted farmgate figure of 4,500 IDR/Kg for dried seaweed the current value to the Kaledupa community is £1,382,400 per annum. Whilst appearing a large sum, when it is viewed on a per family basis their income from seaweed farming is typically £1,152 per annum or £96 per month (1.8 million IDR/month).

One significant way of adding value to the seaweed crop would be to process it on site to make PES (E407a). Whilst creating a new factory may appear a challenging and daunting prospect it also might be feasible and profitable to the community.

The initial issue is to understand the conversion process itself. For commercial reasons, great secrecy exists about the methodology, even now, some 10-15 years since the process was introduced. So far as the author is aware, no standard comprehensive account of the process exists in the literature. It has therefore been necessary to create a sufficiently adequate one from a variety of sources – see Appendix 1.

Some of the most revealing published descriptions come from within Patent Applications. In order to properly describe the novel step of a new invention, the applicant has to place it in the context of existing knowledge ('prior art'). In so doing the applicant, often a large existing manufacturer, has to disclose possibly more than it would wish to. Unless clearly stated in Appendix 1, only such previous knowledge has been used to build up the description of the process, so far as the author is aware.

The essential principle of the process is to have a relatively large shed with a central tracked crane or hoist suspended from the ridge or a suitable beam. Its role is to lift and lower a perforated container, with the seaweed within, through a series of tanks containing the process liquids. One of these needs to be heated. Throughout, only commonplace and easily-sourced chemicals are used.

Since this project covers the Wakatobi area ('Wallacea region') it is desirable to place such a process plant fairly centrally, to minimize journey time and distance for all concerned. Buranga or Langge on Kaledupa may be preferred locations. The pierhead at Buranga may have sufficient space though it may be too close to housing. If approved in the UK, the decision to proceed and choice of precise location must be a matter for consultation with local people, the Forkani and the Wakatobi Park Authorities. World Wildlife Fund (WWF) and The Nature Conservancy (TNC) would need also to be involved.

Whilst the nature and methodology of the process can be reasonably accurately reconstructed from various sources, the economics are under an even greater veil of secrecy and consequently more difficult to glean. However, though slightly dated, sufficient information exists to give a useful insight<sup>(8)</sup>. The following model is based on his account.

Factory buying-in price is typically 1,000 IDR/Kg above farmgate price, this differential being the costs and profit margin of two tiers of sub-regional and regional collectors. The farmers closest to the plant site may immediately benefit from this by delivering their crop in person. Even the more distant ones will cut out the regional collector's buyer's margin and only incur the sub-regional collectors margin of 300 IDR/Kg - so should benefit by about an additional 700 IDR/Kg. Thus the average farmer producing 400Kg/month would instantly gain an extra 280,000-400,000 IDR or £15-21 per month.

The size of the factory is uncertain. There needs to be a consultation with all 1,200 farmers to discover who will be willing to change their existing selling arrangements and supply the new plant. Some may be in debt to their buyers and be contracted to supply them. Others may have cultural reasons for wishing to continue with existing arrangements – the buyers may be relatives or friends from within the community. So it is unlikely that the total production from within the area would, at first, come to the plant. But it is also the case that if a significant proportion does supply the proposed plant, then what is left to the sub-regional buyers may no longer be economic for them to collect and take to Baubau, the sub-regional centre. In any case, these local buyers may still play a role in delivering dried seaweed to the proposed plant from the outer areas of the Wakatobi region.

A cautious assumption might be to design for a plant taking in 3,000 MT/annum i.e. 600 farmers and half of the area's production. The conversion of raw seaweed into product is variously given as 25-33%<sup>(8)(10)</sup>. This figure refers to pure carrageenan. Elsewhere in various patents a greater figure for PES of 43% is quoted (see Appendix 1), which would understandably include the weight of the extra cellulose component found in PES. So, taking this latter figure of 43%, the output of PES might be 1,300MT/annum. Using the previously quoted world price for PES of \$4,650/MT this gives an annual gross production value of \$6.05 million or £2.90 million.

Since the process is known to be cost-effective an assumption of 30% profit margin is made, which would give a gross profit of £870,000 before tax (if any). If this were annually redistributed between the 600 participating farmers it could add £1,450/annum or £120/month to their income, i.e. more than double their average existing income. To this can be added the previously estimated monthly benefit of £15-21 due to enhanced farmgate price.

The provision of a new PES plant would provide much-needed and stable employment within the area by creating new jobs. How many is uncertain. At least two shifts per day would be needed, plus supporting administrative, laboratory and sales staff. An intuitive guess might be between 20-30.

Marketing of PES from Kaledupa should strongly emphasise its production by a community-owned enterprise and thus its 'Fair Trade' credentials.

### **Summary of Recommendations**

1. Consideration is given to the creation of a small factory ('pabrik-mini') for the production of Purified Eucheuma Seaweed to maximise value-added income to local seaweed farmers and to create new jobs.
2. Further investigation of local seaweed-growing procedure is undertaken to ensure its maximum production. If appropriate, further training be given to the farmers.
3. Practical help is given to local seaweed farmers to ensure that drying of their seaweed is optimised.

#### *Note 1:*

*Limitations on water and power are potential issues on Kaledupa.*

*Wherever possible, seawater should be used in the various PES production stages.*

*[The price of electricity for industrial use on the island is 450-460 IDR/kWh or about 2.4p/kWh (this compares favourably with average UK current industrial price of 4.5p/kWh). If existing power supplies are insufficient or discontinuous or considered too unreliable then a modest-sized generator will be required. It must be acoustically clad to reduce noise emission. A typical 50KW standby generator in acoustic enclosure costs about £8,500. For running a generator the local price for diesel is 6,000 – 6,500 IDR/l or about 33p/l and compares with UK red diesel (gasoil) of 42p/l. At half-load, the fuel consumption of the generator would cost about £10,000 per annum, assuming a 16hr day and a 220day year.]*

#### *Note 2:*

*No attempt has been made to calculate the capital cost of creating the proposed PES plant, though its amortised cost is implicit in the profit calculation. It will depend considerably on choice of location and building contractor.*

*Note3:*

*The design of the plant should maximise job creation and minimise energy consumption. Thus a deliberate strategy of reducing mechanisation wherever possible, subject to health and safety considerations, is suggested.*

*Note 4:*

*No discussion of pollution control measures has been made. In such an environmentally sensitive area this will need to be given high priority.*

*Note 5:*

*PES is for human food consumption. It is crucial that the initial factory design and subsequent operating procedures incorporate good manufacturing practices.*

*Note 6:*

*Consideration should be given to also marketing the PES product in China. Indonesia enjoys Special Preferential Treatment Tariff Rate of 8% for carrageenan products (as do all ASEAN countries). The Chinese market for these products is anticipated to grow annually at 13% for the next 5 years <sup>(11)</sup>.*

## **References**

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2. World Aquaculture Symposium 2005
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10. McHugh DJ, ‘Production and Utilization of Products from Commercial Seaweeds’ FAO Fisheries Technical Paper 288 – 1987
11. SEAPlantNet ‘Preliminary Study – Chinese Market for Seaweed’ 2007



## **Appendix 1**

### **A detailed description of the Purified Eucheuma Seaweed (PES or E407a) manufacturing process**

#### **Summary**

Environmentally sensitive production of kappa carrageenan (PES) by the simple processing steps of:

- (a) pre-rinsing carrageenan-containing seaweed to remove surface impurities and contaminants
- (b) cooking the seaweed in a tank containing an aqueous solution of Potassium Hydroxide (KOH) so as to cause desulfation at the 6-position of the galactose units of the carrageenan, and so as to create recurring 3,6 anhydrous galactose polymers by dehydration and reorientation.
- (c) washing the seaweed in a neutralizing bath of dilute Hydrochloric Acid
- (d) washing the seaweed in an optional bleaching step
- (d) rinsing the seaweed in water
- (e) drying and chopping the seaweed into chips or milling into powder

#### **Adapted and modified from:**

1. FAO Fisheries Technical paper 441 'A guide to the seaweed industry' 2003
2. SEAPlantNet - The South East Asia Seaplant Network 'Carrageenan production methods' 2007
3. SuriaLink - The ABC of Eucheuma Seaplant Production 'Basics of alkaline modification' 1-0703-C 2003/2004
4. 'Method for extracting semi-refined carrageenan from seaweed' - United States Patent 5801240
5. 'Process for cultivation of algae' - United States Patent 6858430
6. 'Integrated method for production of carrageenan and liquid fertilizer from fresh seaweeds' - United States Patent 6893479
7. 'Carrageenan-containing product and a method of producing same' United States Patent 5777102

8. 'Carrageenan compositions and methods for their production' United States Patent 6063915

9. 'Process of preparation of biodegradable films from semi refined kappa carrageenan' United States Patent 7067568

10. 'Removal of trace heavy metal contaminants from algae and the carrageenan contained therein United States' Patent 4112223

*Note:*

*For those patents that are still in date (20 years from filing date) only their general descriptions of the process have been used, because these quote 'prior art'. Their novel inventive steps have either not been incorporated or, if mentioned, are made clear in the text.*

*Nevertheless, some of these inventive steps may have a useful contribution to make to any PES process and would require, if the patent is applicable to Indonesia, the seeking of a Licencing arrangement with the inventors and/or their Assignees. Whilst, for simplicity, only US patents are quoted, several also have world coverage under the procedures of World Intellectual Property Organization.*

### **The Process**

A commercial scale method for producing PES should combine traditional simple methods for the semi-refining of kappa carrageenan with optimizing equipment and cycle reduction techniques to provide consistent, robust, high quality, cost-effective production of PES, substantially independently of raw material feedstock variations. Cycle time reductions are achieved by reducing the number and duration of handling points, by consolidating the material handling process through the use of transportable processing baskets for movement of feedstock through the various process steps, and by eliminating or reducing time oriented activities. Cost efficiencies are realized via throughput increases, via the recycling of process fluids, and via process controls based on relative reaction performance, as opposed to reliance on absolute values, such as processing time alone.

The essential goal of the semi-refining process is to improve the gel properties of carrageenan present in seaweed. Carrageenan contains galactose units which are sulfated in the 6-position. These can be converted into 3,6-anhydro galactose units by treatment with a base (alkali such as Potassium Hydroxide - KOH). The resulting carrageenan product containing 3,6-anhydro galactose units exhibits desirable improved gelling and strength properties.

A pre-cursor step of sorting generally refers to the removal of plant materials and other debris to leave only the seaweed that is desired for processing. *Kappaphycus alvarezii* is the preferred raw seaweed feedstock for the production of kappa carrageenan and *Eucheuma denticulatum* for iota carrageenan, and other types of plant material would typically be removed during sorting. If sorting occurs off-site, then bags of dried and sorted full length seaweed will be shipped to the location of carrageenan processing. Testing is preferably conducted to determine the quality of the raw supply of seaweed prior to processing. Information gained regarding the characteristics of the raw starting material will be used at later stage in the process to adjust process controls for cycle times.

*Note:*

*United States Patent 6893479 describes an alternative starting procedure that involves macerating, squeezing and filtering the raw seaweed. This produces a solid feedstock that has a higher yield and quality of PES while at the same time producing a liquor that has excellent plant fertiliser and growth promoter properties.*

It is crucial that each batch of seaweed is true to species. There must be no mixing of (a) *Kappaphycus alvarezii* and (b) *Euचेuma denticulatum*. Such mixing would significantly or totally compromise the final product. Each of these species yield carrageenans that have specific and differing physical and chemical gelling properties. Both seaweed species can be processed by this method – but in entirely separate batches.

*Note:*

*Kappaphycus alvarezii* – was previously and is still commonly (but incorrectly) called *Euचेuma cottonii* and yields kappa carrageenan.

*Euचेuma denticulatum* – was previously and is still commonly (but incorrectly) called *Euचेuma spinosum* (which yields iota carrageenan).

The sorted seaweed is weighed out into pre-determined batch lots for processing. A typical target batch weight would be, for example, 1,000 kg. This is accomplished by loading the seaweed into a processing basket located on a load cell scale. The processing basket is preferably substantially cylindrical in shape and is constructed from a corrosion resistant structural material, such as stainless steel, as are the tanks into which it will be lowered. When the target net batch weight of seaweed is obtained, the loading is stopped. (The seaweed will remain in the single processing basket until after it has been removed from the final rinse, is drained and the seaweed is ready for final chopping, drying and optional further milling.)

It is preferable that the seaweed is chopped into shorter lengths prior to processing. The pre-chopping step increases the surface area available for reaction and improves the homogeneity of the reaction mixture and ultimately accelerates the reaction progress. The pre-chopping step is preferably carried out in a KOH environment, as the potential for carrageenan "leaching" will be lessened. Since kappa carrageenan will precipitate (gel) in the presence of K<sup>+</sup> ions, chopping in the presence of KOH will render the carrageenan insoluble in the water present in the plant materials, thus minimizing losses of carrageenan at this stage. It is preferable to chop the seaweed into lengths of approximately 5-8 inches to reduce process cycle times by exposing an increased seaweed surface area to the alkali modification reaction. The recommended seaweed chop length of approximately 5-8 inches balances the benefits of increased surface area (theoretical optimal chop length being at 1/4" to 1/2") with the carrying/holding limitations of the basket (since optimally finely ground seaweed material will not be retained in the basket). The KOH environment can be achieved by exposing the seaweed to a KOH moisture spray in an enclosed area prior to bringing the seaweed in contact with the knives of a pre-chopper.

The single processing basket containing the batch weight of seaweed is lifted by overhead crane or hoist and is then seated in a seaweed pre-rinse tank for the pre-rinse step. The seaweed pre-rinse tank should preferably contain an aqueous KOH pre-rinse solution which can be obtained as a product recycled from re-purified spent KOH solution generated from cook step, which will be discussed in greater detail below. If

spent KOH solution wash is being re-used in the pre-rinse tank, the expected concentration of such KOH pre-rinse solution would be approximately 4-8%. The water, which maybe seawater, and/or dilute KOH solution, is recirculated through the processing basket during the pre-rinse to dissolve sea salt and Potassium Chloride (KCl) deposits and to wash sand and other particulate matter from the seaweed. Preferably, the seaweed is agitated during this process to enable maximum contact between the pre-rinse solution and the salt residues on the seaweed, and to enable sand and other particulates to be loosened and released from the seaweed.

The processing basket is hoisted by crane from the pre-rinse tank, drained, and then lowered into a cooking tank for the KOH cook step. The cooking tank preferably contains 8-12% by weight KOH aqueous solution maintained at approximately 75°C (minimally 60°C and maximally 80°C). The KOH solution is recirculated through the seaweed in the processing basket to provide agitation of the seaweed. The agitation is beneficial in that it ensures that the hot KOH contained in solution will readily reach the entire batch of seaweed. Preferably the cooking vessel should also be equipped with an agitator, to provide additional mechanical mixing during the cooking process. This can be a simple propeller-type clamp-on stirrer.

Two chemical transformations occur while the carrageenan containing seaweed is subjected to the cooking step in the presence of KOH. The first transformation is desulfation. Desulfation occurs when a sulfate group bonded to the 6-position of the galactose units of a carrageenan polymer molecule is removed by the K<sup>+</sup> ions to form KSO<sub>4</sub> (Acid Potassium Sulphate) in solution. The moderate temperature of the KOH cook sufficiently weakens the tertiary sulfate-galactose bonds to enable the strong K<sup>+</sup> ions from the KOH solution to remove the sulfate group from the galactose by creating potassium sulfate salt, in solution.

The second reaction step is a dehydration of the desulfated product to create the recurring 3,6 anhydrous galactose polymers. The OH<sup>-</sup> ions from the KOH solution, react with the tertiary and secondary bonded H<sup>+</sup> groups at the 3 and 6 positions to form the anhydrous kappa carrageenan polymer plus water.

Subsequently, a reorientation of the polymer occurs to create a more stable geometry. The net result of the two reaction steps and the subsequent reorientation is sulfate removal by ring formation.

The chemical reactions are optimized below the melting point of the carrageenan within the seaweed (at approximately 80°C) and above the minimum dissolution temperature of the carrageenan (which is approximately 60°C). If cooking temperatures are maintained in this range (i.e. between 60 - 80°C), then both steps will readily occur. Through each of these chemical changes, a change in the monitored energy is expected, due to activation energy requirements for each of the reactions.

*Note:*

*The US Patent 5801240 is based on using, at this stage, a redox meter to monitor the process and determine the end-point efficiently. In its absence the duration of cooking will need to be determined by experience. According to the strength of the KOH solution that is used, it will be between 2-3 hours approximately. The choice of temperature will also influence cooking time.*

The refractive index of the aqueous KOH cooking solution can be monitored by conventional means, e.g. a refractometer, in order to track changes in the concentration of salts in the KOH.

Once the reaction equilibrium of the reorientation step has been reached, the KOH cooking process is complete. Typically a cooking time of about 2 hours for 12% KOH w/w, or 3 hours for 8% KOH w/w can be expected. This KOH concentration results in a cook mixture having a pH of between 12-14, which is very corrosive and must be handled with extreme caution. The processing basket is removed from the KOH cooking tank and is allowed to drain solution back into the cooking tank. Upon contact with the carrageenan, the KOH solution will take on a brown, brackish appearance. The pigments which contaminate the KOH will discolour future batches of carrageenan processed in the KOH. Colouration impacts negatively upon the perceived value of the PES product, so efforts need made to limit the extent of colouration due to pigment transfer from the aqueous KOH solution. To that end, the aqueous KOH solution is recirculated through an active carbon filter. In this way, dissolved sugars, cellulose, and seaweed pigments are removed from the KOH solution. The KOH solution can then be titrated to determine its concentration, and then buffered with KOH powder to re-establish an 8-12% by weight KOH solution for the processing of subsequent batches of seaweed. When the KOH solution has been sufficiently spent during the processing of repeated batches of seaweed, it will no longer be practical to filter and buffer the KOH solution for re-use in the cooking tank. The cooking tank will then be refilled with fresh 8-12% by weight KOH solution for further seaweed cooking cycles. The old spent solution can be diluted to form the pre-rinse solution mentioned earlier.

*Note:*

*Euचेuma denticulatum cooking treatment may preferably be undertaken with Calcium Hydroxide (CaOH) at about 7% by weight or Sodium Carbonate (Na<sub>2</sub>CO<sub>3</sub>). The use of Sodium salts for making iota carrageenan appears to be covered in United States Patent 6063915*

It is important from this stage onwards to maintain clean and sanitary conditions to prevent bacterial and fungal re-contamination of the product, if it is to be of 'Food Grade' standard.

The processing basket, after draining, is moved by overhead crane over and lowered into a neutralizing wash tank for the neutralizing step. The wash tank can contain fresh water, or preferably should contain a dilute solution of mineral acid of a type which will not denature the carrageenan. The use of dilute Hydrochloric Acid (HCl) is preferred, as it will significantly decrease the time required for the neutralization of the residual KOH and its removal from the seaweed. The effective wash cycle time can be reduced from between 1-2 hours to less than 1 hour with the use of dilute (approximately 0.1M) Hydrochloric Acid. In order to increase the efficiency of the neutralization process, the pH of the neutralizing wash tank requires monitoring. This can be efficiently carried out using a conventional pH meter. As soon as the desired pH (of approximately 8-9) is reached, the neutralizing process will be stopped by removing the processing basket from the neutralizing wash tank. At this point the crane or hoist will lift the processing basket out of the neutralizing wash tank, which will allow excess wash to drain back in to the tank, and then lower the processing basket into a final rinse tank containing fresh water.

If required, a further bleaching step, using for example, dilute Sodium Hypochlorite (NaClO) solution, can take place at this point to remove undesirable colours from the product.

The final rinse step will remove any significant amount of residual KOH and mineral acid residues from the carrageenan containing seaweed. The spent rinse solution from the final rinse step will be somewhat alkaline, and might also be recycled for use in the pre-rinse step discussed above.

After the final fresh water rinse step, the processing basket is removed by crane, drained, and the seaweed is dumped from the processing basket onto a clean platform. It is placed onto a conveyor belt and is fed into a hammermill with a 2" screen for a wet chop. After wet-chopping, it is then necessary to remove a large quantity of water from the seaweed product by drying. The water content is reduced from approximately 90% to approximately 12%. Mechanical drying means, such as a drum-roller, or a drying centrifuge can be used to force excess water from the seaweed prior to air-drying. The regulatory requirements for food-grade PES are for a moisture content of 12-15% (see Appendix 2). This can be achieved in a variety of ways, usually involving blowing warm dry air through the product, for example, over a grating or in a fluidised bed, or by using a drum-drier. If a lower-value non-food grade product is needed, then outdoor drying on concrete pads is sufficient – it will become contaminated by inert ash, bacteria and fungi.

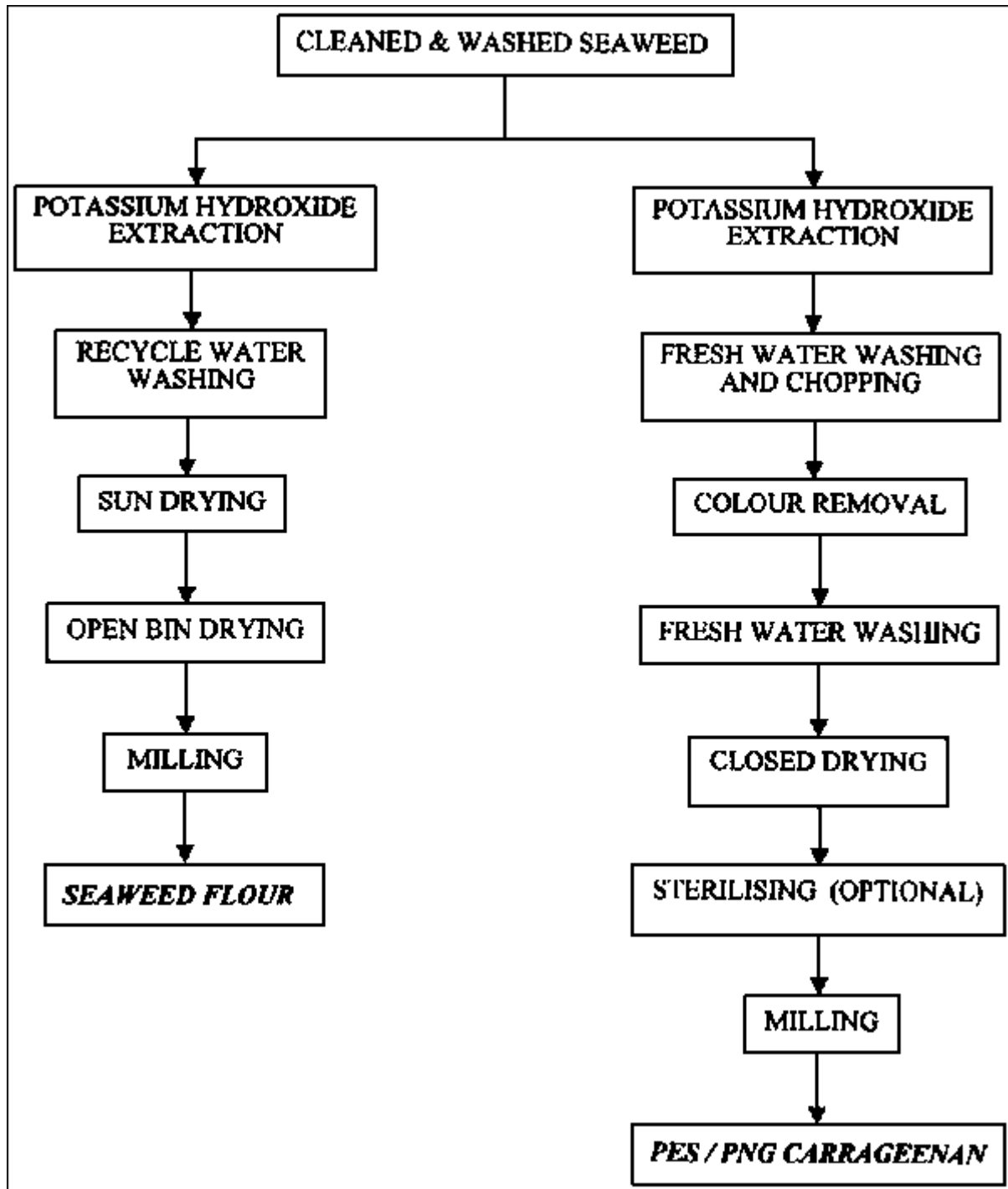
Further processing of the PES product will generally be to particular customer application specifications. For example, it may be further dry chipped and/or milled to a specified particle size. Additionally, the product may be passed over magnets in order to remove any metal impurities prior to being bagged or placed in drums for sale.

The yield for the process is typically in the order of 40 - 45% on dry seaweed basis.

Gel strengths may typically be  $550 \text{ g/cm}^{-2}$  (at 1% solution strength) but will vary according to the quality of the incoming dried seaweed feedstock and the skill and experience of the processing staff.

The chemicals used in the process are commonplace commodities. Nevertheless they should be sourced with care and only 'Food Grade' quality used, to ensure, amongst other issues, that they contain only low or zero levels of heavy metal impurities. This is because the UN, European Union, Chinese and USA, specifications for food grade PES require low heavy metal analyses (See Appendix 2).

**Flow chart for the production of seaweed flour and PES/PNG carrageenans**



Source:

Bixler, H.J. 1996. Recent developments in manufacturing and marketing carrageenan. *Hydrobiologia*, 326/327 pp35-57.

*Note on Flow Chart 1:*

*The use of the term 'Extraction' in the flow chart is incorrect. The KOH acts on the carrageenan within the cellulose matrix of the seaweed and no extraction takes place. Quite to the contrary, active steps are taken to minimize extraction, since this would lead to production losses.*

*Note on Flow Chart 2:*

*PES and PNG are equivalent terms. PNG is 'Philippines Natural Grade'. Seaweed Flour (SF) is typically 'Petfood Grade'.*



## Appendix 2

### International Purity Standards for Purified Eucheuma Seaweed

#### (1) Current European Union PES (E407a) purity criteria, as consolidated in December 2006.

1996L0077— EN— 29.12.2006 — 007.001— 1. This document is meant purely as a documentation tool and the institutions do not assume any liability for its contents

COMMISSION DIRECTIVE 96/77/EC of 2 December 1996 laying down specific purity criteria on food additives other than colours and sweeteners

(Text with EEA relevance)

(OJ L 339, 30.12.1996, p. 1)

Amended by:

Official Journal

No page date

- ▶ M1 Commission Directive 98/86/EC of 11 November 1998 L 334 1 9.12.1998
- ▶ M2 Commission Directive 2000/63/EC of 5 October 2000 L 277 1 30.10.2000
- ▶ M3 Commission Directive 2001/30/EC of 2 May 2001 L 146 1 31.5.2001
- ▶ M4 Commission Directive 2002/82/EC of 15 October 2002 L 292 1 28.10.2002
- ▶ M5 Commission Directive 2003/95/EC of 27 October 2003 L 283 71 31.10.2003
- ▶ M6 Commission Directive 2004/45/EC of 16 April 2004 L 113 19 20.4.2004
- ▶ M7 Commission Directive 2006/129/EC of 8 December 2006 L 346 15 9.12.2006

#### E 407a PROCESSED EUCHEUMA SEAWEED

Synonyms PES (acronym for processed eucheuma seaweed)

Definition Processed eucheuma seaweed is obtained by aqueous alkaline (KOH) treatment of the natural strains of seaweeds *Eucheuma cottonii* and *Eucheuma spinosum*, of the class *Rhodophyceae* (red seaweeds) to remove impurities and by freshwater washing and drying to obtain the product.

Further purification may be achieved by washing with methanol, ethanol or propane-2-ol and drying.

The product consist chiefly of the potassium salt of polysaccharide sulphate esters which, on hydrolysis, yield galactose and 3,6-anhydrogalactose.

Sodium, calcium and magnesium salts of the polysaccharide sulphate esters are present in lesser amounts.

Up to 15% algal cellulose is also present in the product. The carrageenan in processed eucheuma seaweed shall not be hydrolysed or otherwise chemically degraded

## Description

Tan to yellowish, coarse to fine powder which is practically odourless

## Identification

- A. Positive tests for galactose, for anhydrogalactose and for sulphate
- B. Solubility Forms cloudy viscous suspensions in water. Insoluble in ethanol

## Purity

- Methanol, ethanol, propane-2-ol content Not more than 0,1 % singly or in combination
- Viscosity of a 1,5 % solution at 75°C Not less than 5 mPa.s
- Loss on drying Not more than 12 % (105°C, four hours)
- Sulphate Not less than 15 % and not more than 40 % on the dried

## basis (as SO<sub>4</sub>)

- Ash Not less than 15 % and not more than 40 % determined on the dried basis at 550°C
- Acid-insoluble ash Not more than 1 % on the dried basis (insoluble in 10 % hydrochloric acid)
- Acid-insoluble matter Not less than 8 % and not more than 15 % on the dried basis (insoluble in 1 % v/v sulphuric acid)
- Low molecular weight carrageenan (Molecular weight fraction below

## 50 kDa) Not more than 5 %

- Arsenic Not more than 3 mg/kg
- Lead Not more than 5 mg/kg
- Mercury Not more than 1 mg/kg
- Cadmium Not more than 1 mg/kg
- Total plate count Not more than 5 000 colonies per gram
- Yeast and moulds Not more than 300 colonies per gram
- *E. coli* Negative in 5 g
- *Salmonella* spp. Negative in 10 g

<http://eur-lex.europa.eu/LexUriServ/site/en/consleg/1996/L/01996L0077-20061229-en.pdf>

## Note:

*Marinalg, the trade association for carrageenan manufacturers have offered the following opinion:*

*'Presently, there is no validated analytical method available to accurately measure the low molecular weight tail of carrageenan, thereby rendering the European Commission's molecular weight specification very difficult to enforce in a consistent manner.'*

[http://www.marinalg.org/papers/papers\\_inf.htm](http://www.marinalg.org/papers/papers_inf.htm)

## **(2) Specification and test procedures for PES - issued by Joint FAO/WHO Expert Committee on Food Additives (JECFA)**

### 'PROCESSED EUCHEUMA SEAWEED'

Prepared at the 57th JECFA (2001) and published in FNP 52 Add 9 (2001), superseding specifications prepared at the 51st JECFA (1998), published in FNP 52 Add 6 (1998)).

A group ADI "not specified" for carrageenan and processed eucheuma seaweed was established at the 57th JECFA (2001).

### SYNONYMS

PES, PNG-carrageenan, semi-refined carrageenan; INS No. 407a

### DEFINITION

A substance with hydrocolloid properties obtained from either *Eucheuma cottonii* or *E. spinosum* (from the *Rhodophyceae* class of red seaweeds). In addition to carrageenan polysaccharides, processed eucheuma seaweed may contain up to 15% of insoluble algal cellulose and minor amounts of other insoluble matter. Articles of commerce may include sugars for standardization purposes or salts to obtain specific gelling or thickening characteristics. It is distinguished from carrageenan (INS No. 407) by its higher content of cellulosic matter and by the fact that it is not solubilized and precipitated during processing.

The functional component of the product obtained from *E. cottonii* is kappa-carrageenan (a copolymer of D-galactose-4-sulfate and 3,6-anhydro-D-galactose). From *E. spinosum* it is iota-carrageenan (a copolymer of D-galactose-4-sulfate and 3,6-anhydro-D-galactose-2-sulfate).

Processing consists of soaking the cleaned seaweed in alkali for a short time at elevated temperatures. The material is then thoroughly washed with water to remove residual salts followed by purification, drying, and milling to a powder. Alcohols that may be used during purification are restricted to methanol, ethanol, and isopropanol.

### DESCRIPTION

Light tan to white coarse to fine powder

### FUNCTIONAL USES

Thickener, gelling agent, stabilizer, emulsifier

### CHARACTERISTICS

### IDENTIFICATION

## Solubility (FNP 5)

Forms cloudy viscous suspensions in water; insoluble in ethanol

A 1 g sample disperses and partially dissolves in 100 ml of water at 80° giving a cloudy opalescent solution. (The sample disperses in water more readily if first moistened with alcohol, glycerol, or a saturated solution of glucose or sucrose in water).

## Test for sulfate

Dissolve a 100-mg sample in 20 ml of water. Heat to boiling, cool to room temperature, and add 3 ml of barium chloride TS and 5 ml of hydrochloric acid, dilute TS. Filter the mixture. Boil the filtrate for 5 min. A white, crystalline precipitate appears.

## Test for galactose and anhydrogalactose

Proceed as directed under Gum Constituents Identification (FNP 5), using the following as reference standards: galactose, rhamnose, galacturonic acid, 3,6-anhydrogalactose, mannose, arabinose and xylose. Galactose and 3,6-anhydrogalactose should be present.

## Identification of hydrocolloid and predominant type of copolymer

Add 4 g of sample to 200 ml of water, and heat the mixture in a water bath at 80°, with constant stirring until dissolved. Replace any water lost by evaporation, and allow the solution to cool to room temperature. The solution becomes viscous and may form a gel. To 50 ml of the solution or gel, add 200 mg of potassium chloride, then reheat, mix well, and cool. A short-textured ("brittle") gel indicates a carrageenan of a predominantly kappa-type. A compliant ("elastic") gel indicates a predominantly iota-type.

## Infrared absorption

Passes test

## PURITY

### Loss on drying (FNP 5)

Not more than 12% (105° to constant weight)

### pH (FNP 5)

Between 8 and 11 (1 in 100 suspension)

### Viscosity

Not less than 5 cp at 75° (1.5% solution)

### Sulfate

Not less than 15% and not more than 40% (as  $\text{SO}_4^{2-}$ ) on a dry weight basis

Total ash

Not less than 15% and not more than 30% on a dry weight basis

Acid-insoluble ash (FNP 5)

Not more than 1%

Acid-insoluble matter (FNP 5)

Not less than 8% and not more than 15% on a dry weight basis

Use 2 g of sample obtained from part (a) of the procedure for sulfate determination

Residual solvents (FNP 5)

Not more than 0.1% of ethanol, isopropanol, or methanol, singly or in combination

Microbiological criteria (FNP 5)

Initially prepare a  $10^{-1}$  dilution by adding a 50 g sample to 450 ml of Butterfield's phosphate-buffered dilution water and homogenizing the mixture in a high speed blender.

Total (aerobic) plate count: Not more than 5000 cfu/g

*Salmonella* spp.: Negative per test

*E. coli*: Negative in 1 g

Arsenic (FNP 5)

Not more than 3 mg/kg

Lead

Not more than 5 mg/kg

Cadmium

Not more than 2 mg/kg

Mercury

Not more than 1 mg/kg

*Note: Test procedures are omitted for brevity. Full specification can found at:*

<http://www.cybercolloids.net/library/jecfa/index.php?submit=showspec&gum=additive-0830>

### **(3) USA Government specifications for carrageenan**

[Code of Federal Regulations]

[Title 21, Volume 3]

[Revised as of January 1, 2007]

From the U.S. Government Printing Office via GPO Access

[CITE: 21CFR172.620]

[Page 68-69]

#### TITLE 21--FOOD AND DRUGS

CHAPTER I--FOOD AND DRUG ADMINISTRATION, DEPARTMENT OF HEALTH AND HUMAN SERVICES (CONTINUED)

PART 172\_FOOD ADDITIVES PERMITTED FOR DIRECT ADDITION TO FOOD FOR HUMAN

Subpart G\_Gums, Chewing Gum Bases and Related Substances

Sec. 172.620 Carrageenan.

The food additive carrageenan may be safely used in food in accordance with the following prescribed conditions:

(a) The food additive is the refined hydrocolloid prepared by aqueous extraction from the following members of the families Gigartinae and Solieriaceae of the class Rhodophyceae (red seaweed):

Chondrus crispus.

Chondrus ocellatus.

Euचेuma cottonii.

Euचेuma spinosum.

Gigartina acicularis.

Gigartina pistillata.

Gigartina radula.

Gigartina stellata.

(b) The food additive conforms to the following conditions:

[[Page 69]]

(1) It is a sulfated polysaccharide the dominant hexose units of which are galactose and anhydrogalactose.

(2) Range of sulfate content: 20 percent to 40 percent on a dry-weight basis.

(c) The food additive is used or intended for use in the amount necessary for an emulsifier, stabilizer, or thickener in foods, except for those standardized foods that do not provide for such use.

(d) To assure safe use of the additive, the label and labeling of the additive shall bear the name of the additive, carrageenan.

<http://frwebgate.access.gpo.gov/cgi-bin/get-cfr.cgi>

**(4) China 'GB Standards' for Carrageenan \*\*\***

Sulphur Oxide (SO<sub>4</sub><sup>-</sup>) 15 – 40%

Viscosity ≥0.1 Pa.s

Weight loss after drying ≤15%

Total ash content ≤30%

Ash insoluble in acid ≤1%

Lead (Pb) ≤0.001%

Arsenic (As) ≤0.0002%

\*\*\* Prepared by the JLJ Group and International Finance Corporation (World Bank) - 'Preliminary Study - Chinese Market for Seaweed and Carrageenan Industry'

<http://www.seaplant.net/>

### **Appendix 3**

#### **Carrageenan uses**

Before discussing uses, some explanations of the properties of carrageenans are necessary.

Both kappa and iota carrageenan form gels with potassium and calcium salts. Aqueous solutions of both carrageenans must be heated above 60°C for the carrageenan to dissolve, and after addition of the salt, the gel forms as the solution cools. For kappa, as little as 0.5 percent in water and 0.2 percent in milk is sufficient to form gels.

Kappa forms gels most strongly with potassium salts, followed by calcium salts. Potassium gives a rigid, elastic gel while calcium produces a stiff, brittle gel. Kappa gives the strongest gels of all carrageenans, but they are also the ones most likely to bleed (most subject to syneresis). This liability can be lessened in a couple of ways. If iota and lambda carrageenans are blended in with the kappa, bleeding can be reduced, so will also the rigidity and brittleness of the gel; however, the gel strength may also be lowered. Syneresis can also be reduced by adding locust bean gum obtained from the seeds of the carob tree. This gum also allows the amount of kappa to be reduced while still maintaining the same gel strength. The kappa can be reduced to one-third of the concentration that would be needed if no locust bean gum were used. The resulting gels are more resilient than those with kappa alone. As long as locust bean gum is cheaper than kappa there is also an economic advantage. However, the cost of locust bean gum can fluctuate depending on the harvest and demand.

Iota forms gels most strongly with calcium salts, followed by potassium salts - the reverse of kappa reactivities. Calcium gels are soft and resilient and are virtually free of bleeding. They can be frozen and thawed without destroying the gel. They show an unusual property for a gel - thixotropic flow; this means the gel can be stirred and it will flow like a thick liquid, but if left to stand it will gradually reform a gel.

A similar thixotropic behaviour is found with very low concentrations of kappa carrageenan in milk; a weak gel forms that is easily made to flow by shaking. The weak gel is strong enough to suspend fine particles in the milk, such as cocoa in chocolate milk.

Protein reactivity of carrageenans is an important property that is utilized in several applications. Carrageenan molecules carry negative charges; this is what enables them to combine with positively charged particles like the potassium found in potassium salts. They can also combine with positively charged proteins. Carrageenan will combine with the protein in milk (casein) to form a three-dimensional gel network. The exact nature of the interaction of proteins with carrageenans appears to be more complex than this simple explanation.



## **Dairy products:**

The main applications for carrageenan are in the food industry, especially in dairy products.

Frequently, only very small additions are necessary, 0.01-0.05 percent. For example, kappa carrageenan (at 0.01-0.04 percent) added to cottage cheese will prevent separation of whey, and a similar amount added to ice cream also prevents whey separation that may be caused by other gums that were added to the ice cream to control texture and ice crystal growth. The cocoa in chocolate milk can be kept in suspension by addition of similar amounts of kappa; it builds a weak thixotropic gel that is stable as long as it is not shaken strongly. Dry instant chocolate mixes, to be mixed with water or milk, can have improved stability and mouth feel using lambda or a mixture of carrageenans.

Lambda or a mixture can also improve liquid coffee whiteners by preventing the separation of fat; these applications require 0.2-0.3 percent additions, but much smaller quantities will prevent fat separation in evaporated milks. Those small containers of UHT sterilized milk found in the refrigerators of some hotels may have kappa added to prevent fat and protein separation. Lambda or kappa may be added to natural cream to help maintain the lightness (incorporated air) if it is whipped. Many more uses in milk and dairy products can be found in the references below.

## **Water-based foods:**

With the appearance of bovine spongiform encephalopathy (BSE, or mad cow disease) and foot-and-mouth disease, efforts have been made to find suitable substitutes for gelatin. Gelatin jellies have long been favoured because they melt at body temperature, giving a smooth mouth feel and easy release of flavours. However, if they are stored for a day or two, they toughen and are less pleasant to eat. Gels made from iota carrageenan have the disadvantage of a high melting temperature, so they are not as smooth to eat as gelatin gels. They do not melt on hot days and do not require refrigeration to make them set, so these are advantages in hot or tropical climates, and a further advantage is that they do not toughen on storage. In the last two years there have been several claims by food ingredients companies for products, made from a mixture of hydrocolloids, that imitate the properties of gelatin. Carrageenan producers find that by combining various carrageenans with locust bean gum, konjac flour and starch, they can provide a variety of melting and non-melting gels and gel textures to meet the requirements of most of their clients. Long-life refrigerated mousse desserts, based on carrageenan and pectin rather than gelatin, are suitable for vegetarians and some ethnic groups.

Conventional fruit jellies are based on pectin and a high sugar content to help set the jelly. In a low- or non-calorie jelly the pectin must be replaced, and mixtures of kappa and iota have proved to be suitable. Fruit drink mixes to be reconstituted in cold water contain sugar (or aspartame), acid and flavour. Addition of lambda carrageenan gives body and a pleasant mouth feel. Sorbet is a creamy alternative to ice cream with no fat; use of a mixed kappa and iota together with locust bean gum or pectin provides a smooth texture to the sorbet.

Low-oil or no-oil salad dressings use iota or kappa to help suspend herbs, etc., and to provide the mouth feel that is expected from a normal salad dressing. The low oil content of reduced-oil mayonnaise normally gives a thin product, rather like a hand lotion; additives are needed to thicken it and to stabilize the oil-in-water emulsion. A combination of carrageenan and xanthan gum is effective. Xanthan gum is made by a bacterial fermentation process; its development was pioneered in the early 1960s by the Kelco Company, then the largest producer of alginate; it is now an accepted and widely used food additive.

### **Beer fining:**

The ability to interact with protein makes carrageenan an excellent beer kettle-fining agent. Kappa carrageenan is negatively charged in the solution, owing to its sulphate groups. Wort proteins interact in these charged sites. At very low dosage, carrageenan stick together particles present such as protein, polyphenols and polysaccharides. These form large aggregates in wort which settle faster and are easier to filtrate.

### **Meat products:**

In preparing hams, addition of carrageenan to the brine solution used in pumping improves the product because the carrageenan binds free water and interacts with the protein so that the soluble protein is retained. For successful penetration, the brine solution must have a low viscosity, but dissolved carrageenan would increase the viscosity. The carrageenan is therefore dispersed in the water after the brine salts are added; the carrageenan does not dissolve because of the high salt concentration, but as the ham cooks it does dissolve and is then effective.

There is a growing consumer demand for pre-cooked poultry products such as chicken and turkey pieces. Poultry processors were concerned about the loss of water during cooking (this lowered their yield per unit weight of product) and the loss in texture and eating quality that resulted. By injecting a brine containing salt, phosphate and carrageenan into the muscle of the meat, these problems are overcome. As the meat cooks, the carrageenan binds water within the poultry muscle and improves texture and tenderness. The processors are pleased because they now have a higher yield; in fact they find that they can even add some extra water to the poultry and it will be retained. The consumer receives a better product. The carrageenan producer is pleased because about 0.5 percent carrageenan is added, much more than the 0.05-0.1 percent used in dairy products. The future looks bright for this kind of application in meat products.

Hydrocolloids are being tried as fat replacements in low-fat products, with varying degrees of success. When fat or salt are reduced, meat and poultry can suffer loss of tenderness, juiciness and flavour. Low-fat products formulated with phosphates and carrageenan can have the juiciness and tenderness restored. Kappa carrageenan has been used with some success in replacing half the normal fat in frankfurters. Reduction of fat in ground meat products like hamburgers results in a different mouth feel and dry taste, which consumers do not always accept. Iota can be mixed with fresh ground beef and when cooked it provides fat-like characteristics and moisture retention that make the product more acceptable. This was the basis for McDonald's "MacLean" hamburger.

**Pet food:**

This is the largest application for seaweed flour, using about 5,500 tonnes annually (2003). Refined carrageenan could also be used, but its cost is too high and seaweed flour is about one-quarter of its price. Seaweed flour becomes an even better proposition because when combined with locust bean gum, less carrageenan is required, but this combination still gives an excellent product and it is very affordable. The meat used in canned pet foods is usually waste cuts from the abattoir. It is chopped into chunks or smaller pieces, mixed with water, flavours, seaweed flour (kappa carrageenan) and locust bean gum, canned and cooked. The two hydrocolloids help to bind the meat together and, depending on the concentrations used, either provide a thickened gravy around the meat pieces or a flavoured jelly, either of which enhances the appearance of the product as it is removed from the can. Konjac (or konjaku) gum, made from the konjac tuber or elephant yam (*Amorphophallus konjac*), can be used in place of locust bean gum. Konjac gels are clearer than locust bean gels and can help with costs when the price of locust bean gum rises, as it does occasionally.

**Air freshener gels:**

When you need to improve the odours in your room, air freshener gels are one of the products available at supermarkets. They are made from kappa carrageenan, a potassium salt, water and perfume. When mixed, the perfumed gel forms and it is moulded to a shape to fit the holder. When purchased, the holder is sealed; to use, the holder is opened slightly and the moisture plus perfume are gradually released from the gel. Eventually the gel dries out leaving a small residue in the holder, which is then discarded. About 200 tonne/year of seaweed flour grade of carrageenan is the estimated consumption for this application.

**Toothpaste:**

The essential ingredients in toothpaste are chalk or a similar mild abrasive, detergent, flavour, water and a thickening agent that will provide enough body to the paste to ensure that the abrasive is kept in suspension and that there is no separation of water. A thixotropic thickener is preferable, i.e. that has gel-like properties when allowed to stand but that will flow when pressure is applied to it. Iota carrageenan, at about 1 percent, is one of the most useful thickening agents, it meets the above criteria and gives a paste that is easily rinsed from the toothbrush. When the size of the toothpaste market is considered, even at 1 percent concentration this represents a large market for iota.

**Immobilized biocatalysts:**

Many commercial chemical syntheses and conversions are best carried out using biocatalysts such as enzymes or active whole cells. Examples include the use of enzymes for the conversion of glucose to fructose, the production of L-amino acids for use in foods, the synthesis of new penicillins after hydrolysis of penicillin G, the use of whole cells for the conversion of starch to ethanol (for beer brewing), and the continuous production of yoghurt. To carry out these processes on a moderate to large scale, the biocatalysts must be in a concentrated form and be recoverable from the process for re-use.

This can be achieved by "immobilizing" the enzymes or cells by entrapping them in a material that will still allow penetration by the substance to be converted or changed. Originally, single enzymes were isolated and used for a specific conversion, but now similar or better results can be obtained using whole cells, and this is more economical. An added advantage of immobilization is that the cells last longer. Ordinary suspended cells may have good activity for only 1-2 days, while immobilized cells can last for 30 days. Beads made with calcium alginate were one of the first materials to be used for immobilization. The whole cells are suspended in a solution of sodium alginate and this is added dropwise to a calcium chloride solution. The beads form in much the same way as described for artificial cherries. In use, they are packed into a column and a solution of the substance to be converted is fed into the top of the column and allowed to flow through the bed of beads containing the immobilized biocatalyst in the cells. The conversion takes place and the product comes out at the bottom. A simple example is to immobilize yeast cells, flow a solution of sugar through the beads, and the sugar is converted to alcohol.

Carrageenan gels are a medium for immobilizing enzymes or whole cells. Kappa carrageenan gives the strongest gels and beads made from this show sufficient mechanical strength for packing in columns, and yet they are permeable to most substances.

**Carrageenan markets (2001):**

Application	tonnes	%
Dairy	11 000	33
Meat and poultry	5 000	15
Water gels	5 000	15
PES food grade	8 000	25
Toothpaste	2 000	6
Other	2 000	6
Total	33 000	100

Adapted from:

'A guide to the seaweed industry'

FAO Fisheries Technical Paper 441

McHugh DJ 2003