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Review Paper

Industrial and Non-food Uses for Carrageenan

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ABSTRACT

Industrial and non-food uses of carrageenan are discussed in relation to the properties of carrageenan. Specific areas that are covered include slurry stabilization and suspension, interaction with polyols, and entrapment/immobilization. The applications range from dentrifrice preparations to anti-icers.

INTRODUCTION

The carrageenan family of polymers consists of linear-sulfated polysaccharides of D-galactose and 3,6-anhydro-D-galactose (3,6-AG) (Glicksman, 1983) extracted from red algae (Rhodophyceae). The viscoelasticity of the gelling carrageenans is sensitive to both the nature and concentration of cations. Indeed, in liquid systems not containing proteins, the functionality of a given carrageenan is critically dependent on the ionic environment (Tye, 1988). Of the three idealized carrageenans, lambda is the least salt sensitive and kappa the most. By blending carrageenans, the viscoelasticity of the sol and gel phases can be varied to suit a wide variety of applications.

Commercially available carrageenans are essentially ground, dehydrated gels containing approximately 7% water, much of which is complexed (hydrogen-bonded) to the polysaccharide molecule, an important factor in their structural stability (Gekko *et al.*, 1985). The texture, stability and functionality of a product stabilized with carrageenan is largely determined by the viscoelasticity imparted to the system by the hydrated carrageenan. In cold water, carrageenan powders

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absorb water to a greater or lesser extent, softening and swelling in the process. Generally, the higher the 3,6-AG content and the lower the ester sulfate level, the less readily will the carrageenan hydrate. Hydration and solubility of kappa and iota carrageenan can be enhanced by ion exchanging the carrageenan to give a material predominantly in the sodium form. Carrageenans are not susceptible to cellulase enzyme attack.

Following World War II, expansion in the food industry coupled with the need for convenience foods and an increased awareness of quality, produced a demand for stabilizers capable of modifying and controlling texture and rheology. An intimate relationship quickly developed between the food and gums and stabilizer industries. At the present time, some 70% of all carrageenan products are utilized by the food industry. Of the remaining commercially used products, the major applications are in the cosmetics and personal care industries, especially toothpaste. A novel application in the personal care industry has been recently introduced by a major marketer of men's aerosol shaving creams for sensitive skins.

It is the purpose of this discussion to expand on the non-food uses of carrageenan with particular reference to the new and novel applications which are currently being researched and developed by a variety of unrelated industries. The common thread is the properties and interactions of carrageenan in aqueous electrolyte systems which may or may not contain polyols and dispersed pigments.

DENTIFRICE

Although people have cleaned their teeth one way or another for thousands of years, doing it regularly with toothbrush and dentifrice was just becoming a widespread habit 50 years ago. The modern dentifrice system is a complex mixture of inorganic and organic compounds suspended in a continuous phase and stabilized by a hydrocolloid which is often referred to as a binder by toothpaste manufacturers (Tye, 1985). Since 1950, considerable effort has been expended in developing therapeutic dentifrices which will not only clean efficiently but will also convey pharmacologically active substances to the tooth surface or environment (Vond de Fehr & Moller, 1978). Carrageenan has been successfully supplied to the industry for more than 30 years and is considered by many as the best functional stabilizer for dentifrice systems.

Carrageenans stabilize toothpaste with a combination of viscosity, continuous-phase gel formation and by acting as a dispersant for the abrasive (a property which is exploited in the stabilization of high solid slurries and industrial suspensions). The continuous-phase gel matrix formed by carrageenan binders not only enhances viscosity stabilization but also provides the clean break (non-tailing, non-stringy) characteristics of these pastes.

Specific interactions with the surface of abrasives (including silica) provide a mechanism for the coating of abrasive particulates which maintains separation between the particles, preventing drying out and hard plug formation in tubes and pump packages.

Carrageenan stabilization

The physical interactions in the toothpaste system determine a carrageenan's hydration characteristics, gelation potential and viscoelasticity of the continuous-phase gel. It is these properties which define the binder's functionality in a particular formulation and process sequence. It is convenient to think of a toothpaste in terms of the abrasive, polyol humectant and ionic environment and their interaction with the carrageenan binder.

The interactions of carrageenan with pigments such as calcium carbonate, dicalcium phosphate and silica (much used as abrasives in the dentifrice industry) is considered in detail in the paragraphs dealing with industrial suspensions. Polyols and their association with carrageenan are discussed under the section on anti-icers.

Toothpaste stability

Hardening and separation are nightmares which keep toothpaste manufacturers awake at night. The introduction of pump packaging exacerbated problems associated with hardening and separation. Some hardening in a tube of toothpaste can be tolerated since the customer is unaware of the problem; he/she does not measure the amount of force required to extrude the paste from the tube. With pumps, however, the mechanism is sensitive to the force required to start the flow of the paste. Hardening can lead to pump failure, customer complaints and loss of market share. Typically, carrageenan-based toothpastes build their structure very quickly and attain in excess of 95% of their viscosity within the first few hours of manufacture. Toothpastes prepared with CMC and xanthan gums continue to thicken over the lifetime of the paste (Fig. 1). Rotating cylinder rheograms of finished pastes show the carrageenan systems to have considerably lower yield points than other systems (Fig. 2), a desirable property both from a manufacturing standpoint and for the design of pump packages.

Separation is the term used when the water–humectant–flavor oil appears as a separate phase. Typically, the customer will notice a

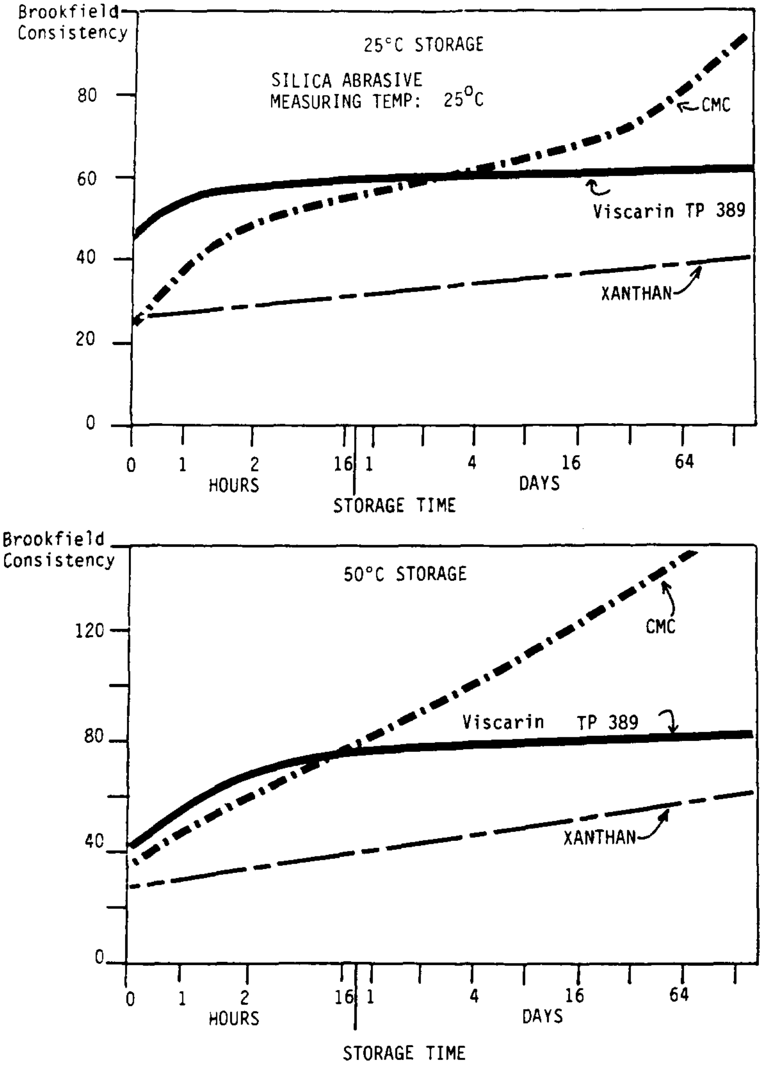

Fig. 1. Long-term stability of Viscarin TP 389 carrageenan, CMC and xanthan-based toothpastes. Brookfield consistency measured with a Brookfield Helipath at 2·5 rev/min 'C' bar. Viscarin TP 389 is a trade name for a cold-water-soluble carrageenan blend, FMC Corporation. Brookfield is a trade name of Brookfield Engineering Laboratories Inc.

yellowish oily liquid when the cap is removed from the tube or pump. Again pumps pose greater problems than tubes. In the latter packages, liquid separation, if present, tends to collect at the bottom of the tube and may be unnoticeable; with pumps it will collect at the top and be very

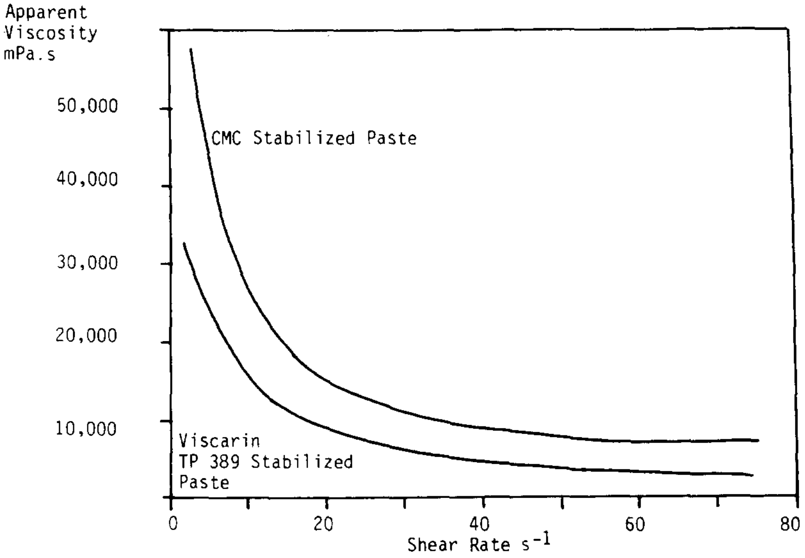

Fig. 2. Shear thinning profiles of freshly prepared silica toothpaste stabilized with CMC and Viscarin TP 389 carrageenan.

noticeable. Separation is controlled by selecting the carrageenan with regard to the nature of the abrasive and ionic environment. The ionic environment is discussed in more detail below.

Using carrageenan in dentifrice preparations

A carragenan's hydration characteristics are critically dependent on the ionic environment. Figure 3 illustrates the effect varying levels of Na^+ have on the swelling and hydration characteristics of a typical iota carrageenan binder. Increasing the ionic concentration decreases cold water swelling and pushes the solvation temperature to higher values. The ionic effects depend upon the cations and not on the anions, which is not surprising in view of the fact that the carrageenan molecule bears negative sulfate groups.

Typically, dentifrice preparations are made hot (the mixing vats are actively heated to around 60°C) or cold (no heat is applied to the vats which warm to around 35°C from the mixing). For hot processing, the carrageenan can be added to the water–humectant system along with the salts. For cold preparation, the gum must be hydrated before addition of the salts. It can be seen from the hydration profiles that, even in hot processes, toothpastes are stabilized predominantly by swollen particles

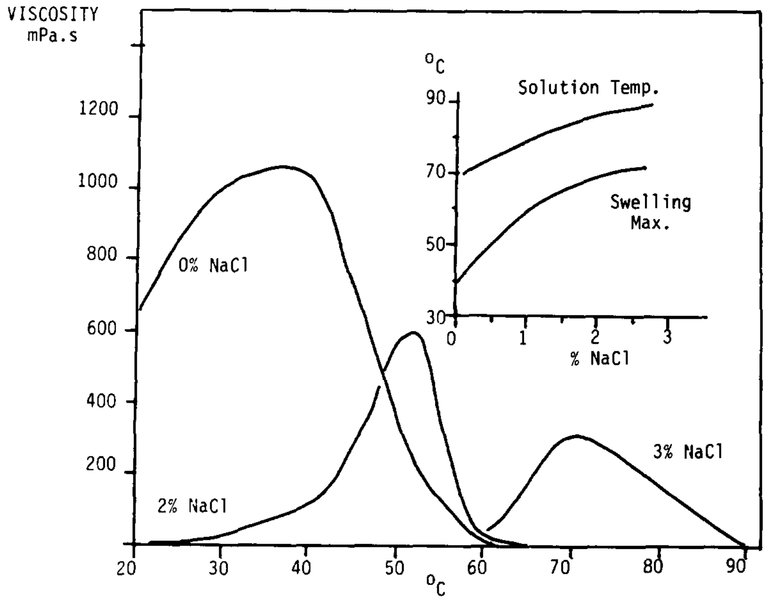

Fig. 3. Effect of sodium on the hydration of Viscarin TP 389 carrageenan.

of carrageenan rather than solution phase material. The swollen particles must have the correct viscoelasticity to form a coherent gel structure. If this is not the case, a grainy and poorly stabilized paste results as happens if a kappa carrageenan is used.

The nature of the cation is of considerable significance with regard to both the hydration and performance of a given binder. Figure 4 shows the response of an iota carrageenan to sodium and potassium (the profiles were obtained using a Brabender™ Amylograph, C. W. Brabender Instruments, Inc.). Potassium promotes a tighter gel structure than sodium which can lead to separation in toothpastes containing potassium and stabilized with a traditional carrageenan binder.

Demands on the hydrocolloid increased dramatically with the introduction of high salt and potassium containing antitartar systems. Binders which were perfectly adequate for the earlier generations of toothpaste suddenly became inadequate. Customer needs have prompted the carrageenan industry to respond with new products which have a much greater tolerance to salts and in particular to potassium, than the traditional binders used for toothpaste (Marine Colloids 1988). Figure 5 shows the response to potassium of one such binder as recorded on a Brabender Amylograph in which the system was heated to 70°C prior to thermal transport to ambient temperature.

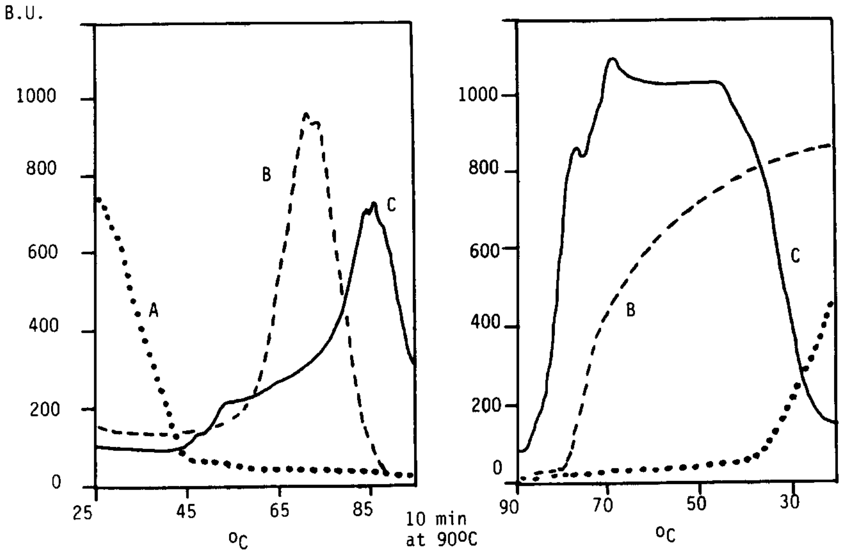

Fig. 4. Heating and cooling rheologies of Viscarin TP 389 carrageenan in the presence of Na$^+$ and K$^+$. Viscosity is in Brabender units. 2% Viscarin TP 389 in (A) distilled water, (B) NaCl solution and (C) 3% TKPP solution.

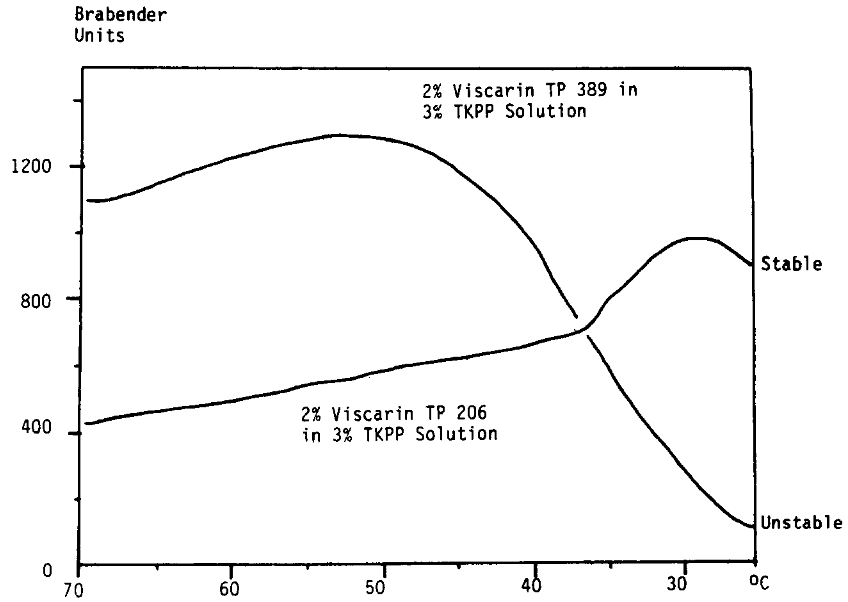

Fig. 5. Cooling rheology of Viscarin TP 206 carrageenan in the presence of K$^+$ compared with Viscarin TP 389. Viscarin TP 206 is a trade name for a cold-water-soluble carrageenan.

Compatability with other gums

Carrageenans are compatible with all neutral and anionic gums and show a positive synergism with some — e.g., with locust bean gum. Being negatively charged, carrageenans can precipitate out in the presence of positively charged compounds such as quaternary ammonium compounds. (However, the interaction with the casein micelle leads to many dairy applications for carrageenan.)

Future trends

Following the introduction of fluoride-containing toothpastes, the industry enjoyed many years without drastic change. The introduction of antitartar preparations and novel packaging concepts has drastically changed that picture. All the major toothpaste companies are actively conducting research on many novel formulations which will further tax the ingenuity and innovation of the gum industry.

INDUSTRIAL SUSPENSIONS AND SLURRIES

Carrageenan interacts strongly with common pigments such as calcium carbonate and dicalcium phosphate, silica and alumina. In fact, iota carrageenan will act as a dispersant for calcium-based pigments at high solids (70–72%). Figure 6 shows that iota carrageenan is a more effective dispersant than Dispex™ N 40 (Allied Colloids Ltd) polyacrylate up to aqueous gum concentrations of around 0·3% w/w. At higher gum levels, a continuous-phase gel structure becomes apparent and the system resembles a well-stabilized soft-flock with a low yield point.

Iota carrageenan is well suited to the stabilization of pigment dispersions and slurries both for tank car and pipeline transportation.

Tank car transportation

The idea of the tank car transportation of solids in the form of an aqueous high-solids slurry is not new (Flintkote Bulletin, 1978). The design of a slurry storage and distribution system is relatively straightforward, so long as the slurry characteristics are taken into consideration. The yield point and thixotropy of a given slurry are of prime importance. Slurries are transferred to storage tanks from rail car or tank truck by pump or air pressure. Typical centrifugal pumps have a 400 liter/min capacity against a 15-m head through a 10-cm loading line.

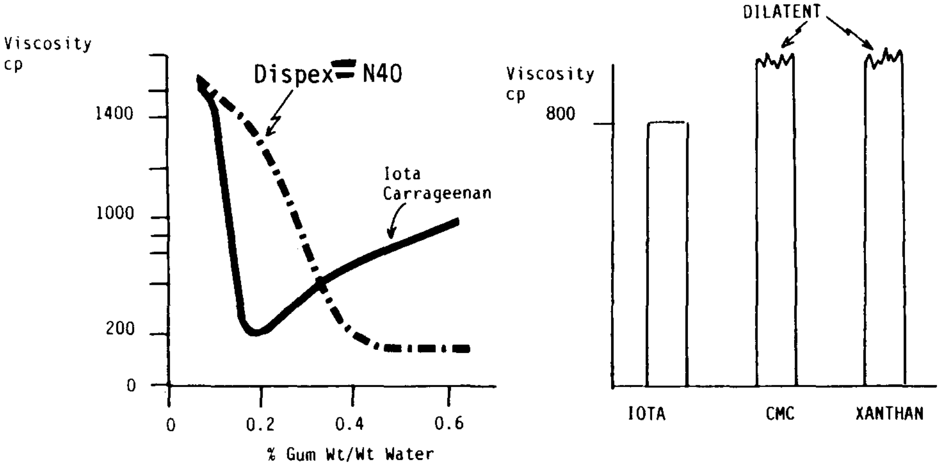

Fig. 6. Iota carrageenan as a dispersant for calcium carbonate and dicalcium phosphate. Solids loading: 70% freshly prepared. Dispex N 40 is a trade name for a polyacrylate.

Storage tanks are stirred intermittently — about 15 min/h at 20 rev/min. Distribution to use points is done at a velocity of 0·5–2 m/s via recirculation loops with long radius bends and no vertical standpipes. Slurries are not allowed to stand in the circulation loops. The hydrocolloid used for viscosity reduction and stabilization must be shear stable under the conditions encountered during transfer and in the distribution loops.

Shear stability

Many industrial applications require polymer molecules to be stable during pumping operations. Although all polysaccharides will undergo degradation at sufficiently high shear rates (for example, under the sonic shearing conditions of ASTM D2603-76), carrageenan seems to be one of the most stable.

The stability of calcium carbonate slurries dispersed with Dispex^{TM} N 40 and stabilized with iota carrageenan is not decreased after 8 min shearing on a Sorvall^{TM} Omni Mixer (E.I. Du Pont de Nemours & Co.) rotating at 20 000 rev/min approximately equivalent to 1700 m/min (Tye, 1981). Rotating cylinder rheograms, generated by a Fann^{TM} viscometer (NL Industries, Inc.) for 72% solids dispersions are shown in Fig. 7. Figure 8 gives the apparent viscosity (expressed as dynes/cm/sec) at viscometer rotation speeds of 300 and 600 rev/min. The fall in apparent viscosity with time in the Omni Mixer suggests that the slurry is not fully dispersed at the onset of shearing. The small increase after about 6 min in the mixer probably results from polymer degradation.

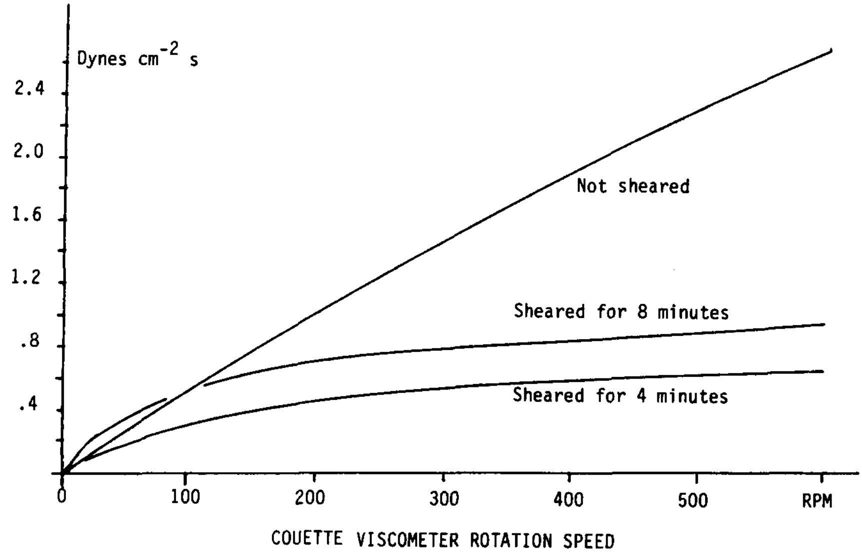

Fig. 7. Effect of shear on calcium carbonate slurries. Couette viscometer rheogram of slurries after shearing. 72% solids, 0·55% Dispex N 40. Shearing device: Omni mixer rotating at 20 000 rev/min. Viscometer: Fann, large bob, large rotor, 25°C.

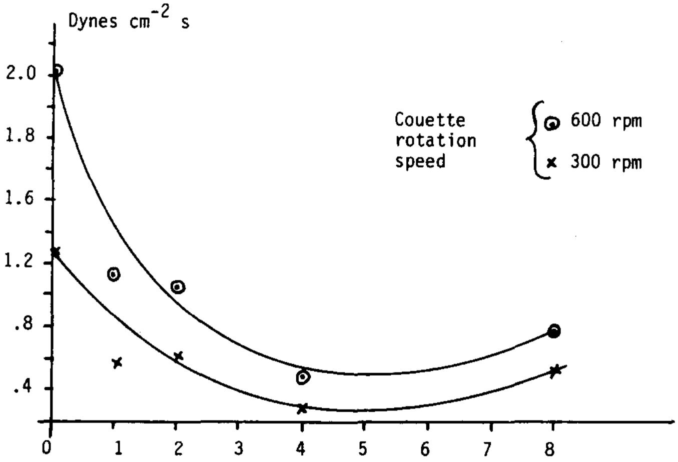

Fig. 8. Effect of shear on calcium carbonate slurries. Couette viscometer readings taken after shearing on an Omni mixer rotating at 20 000 rev/min. Viscometer: Fann, large bob, small rotor.

Transportation of iron oxide slurries

Black iron oxide is currently transported in tank cars from the pigment manufacturers to the makers of black bricks and tiles. Carrageenan interacts very strongly with transition metals and very effectively coats and stabilizes iron-based pigments at 62% solids. It has been shown to be a much more efficient stabilizer than CMC which, although an industry standard for many years, has significant deficiencies particularly during hot weather. Carrageenan systems can have an aqueous gel structure (depending on the nature of the carrageenan and the ionic environment) with a sol–gel transition above the maximum temperature likely to be experienced in a tank car.

Liquid scouring cleansers

There is active interest by major brand name manufacturers and private label houses in producing a liquid scouring cleanser product for use on fiberglass, plastics, tiles and other easily abraded surfaces. The concept of such a cleanser dates from the late 1970s when Lever Brothers test marketed 'Liquid Vim' and then withdrew the product. Since then, several other liquid cleansers have appeared.

Liquid scouring cleansers are basically suspensions of a dense but mild abrasive such as calcite with detergents and suspending/and dispersing agents — they are low solids slurries and if free of oxidizing agents can be stabilized with a polysaccharide such as a carrageenan. Iota-based stabilizers impart good functional properties such as temperature and storage stability outperforming other gums such as CMC and xanthan. The iota systems form thixotropic gels with a rapid build-up of structure after shearing which contrasts with the lower yield point of xanthan systems. The yield points of a carrageenan system result from disruption of the three-dimensional polymer network which serves to maintain particle separation aiding stability. CMC slurries (including dentifrice) often show a yield point whose origin lies in the energy required to disrupt settled solids. With non-gelling polymers, the appearance of a yield point indicates instability and is most undesirable.

Hydraulic seeding

Grass seed, mixing with fertilizer, cellulose, water, a tackifier agent and a hydrocolloid, is sprayed onto banks and large projects as an efficient means of seeding during landscaping operations following major construction work (Buckingham, 1987). The hydrocolloid is present to suspend the grass seed and fertilizer prior to pumping and to help retain the seed on the soil. Carrageenan is especially useful in this application and has been found much easier to work with than the guar gum used previously (FMC Corporation, 1988).

Ceramic coatings

Carrageenan is being used currently by at least one major spark plug company as a carrier for ceramic coatings during the manufacture of automotive spark plugs.

ANTI-ICERS

Ethylene glycol and other polyols have long been used in aqueous solutions of various strengths for removing ice and snow accumulation from machinery and functional surfaces such as aircraft wings. In the absence of a thickening polymer, the glycol solutions soon drain from the surfaces and thus provide no long-term protection. An anti-icing fluid, on the other hand, contains a polymer to thicken the fluid so that it remains on the treated surface.

Two types of fluid in current use for aviation applications are the non-thickened de-icers (type I fluids) and the thickened anti-icers (or type II fluids). An anti-icer designed for aircraft should form an essentially continuous film coating, after its application by conventional spraying devices, even on nonhorizontal surfaces and should provide long-term protection against ice or snow accumulation. It is essential that the anti-icer fluid is blown off the wings during the aircraft's run-up to take off (prior to aircraft rotation).

The protection of exposed heavy machinery requires a thick coating which is resistant to wind shear over long periods of time and yet will not clog or interfere with moving parts. Ideally, such a coating should also contain corrosion inhibitors and lubricants and be easy to apply and remove. For all anti-icing applications, the system must be nontoxic and harmless to the environment, which puts severe limitations on the types of thickening polymers which can be used.

Carrageenans interact strongly with polyols to give systems with unique rheological properties which can usefully control the flow and cling properties of any system containing a polyol. Carrageenans are nontoxic food grade materials and pose no threat or hazard to the environment and are thus ideally suited to thickening polyol systems.

Glycol–water–carrageenan systems exhibit a definite yield point followed by marked shear thinning which can be utilized to give very effective industrial (spray-applied) de-icers ranging from aircraft to heavy machinery. Carrageenan gel matrices readily entrap a wide variety of pigments and oils from heavy hydrocarbon to light and volatile flavor systems thus enabling the easy inclusion of corrosion inhibitors and lubricants. (The entrapment of inert and active materials is discussed further below.)

Na^+-K^+ iota carrageenan is soluble in hot glycerine and ethylene glycol but not in propylene glycol propan-1,3-diol or any other polyol with a hydroxyl content (OH mol. wt) less than around 0·53 (Tye, 1987). As in aqueous systems, the solvation characteristics of a carrageenan in a particular polyol–water system are critically dependent on the cation balance. Thus an iota carrageenan which is predominantly Na^+/Ca^{2+} will not dissolve in any dry polyol at temperatures up to 95°C. Typically, carrageenans can be dissolved in water–polyol mixes but the water–polyol ratio required for coagulation of the carrageenan depends on the carrageenan, polyol and ionic environment.

Although both yield point and viscosity increase rapidly as the iota concentration increases, the systems maintain their thixotropy with very marked shear thinning. For example, a solution of 0·2% sodium iota in dry glycerine will be gelled when quiescent and yet will flow readily when subjected to low shear (Fig. 9). Kappa carrageenans in water–polyol systems form gels with well-defined and measurable fracture values. Figure 10 shows a typical Instron™ (Instron Corporation) gel breakforce profile for water–glycerine–kappa carrageenan systems at constant gum concentration as a function of water–glycerine ratio. The gel breakforce passes through a maximum which represents the water–polyol ratio at which coagulation of the carrageenan just begins. The shear thinning properties which make carrageenan-thickened glycol fluids applicable for aircraft anti-icing are shown in Fig. 11 (Tye *et al.*, 1987).

COSMETIC APPLICATIONS

The unique interactions between carrageenan and polyols can be exploited to control textural properties of any formulation or preparation containing polyols. This is especially true of complex cosmetic hand lotions and conditioners which are subject to considerable constraints on the ingredients and their concentration. Figure 12 shows an organoleptic profile for carrageenans in water–polyol systems as a function of water–polyol ratio and carrageenan concentration.

ENTRAPMENT

Any species, solid or dissolved, present in a kappa carrageenan solution will be trapped in the gel matrix formed when the carrageenan is induced

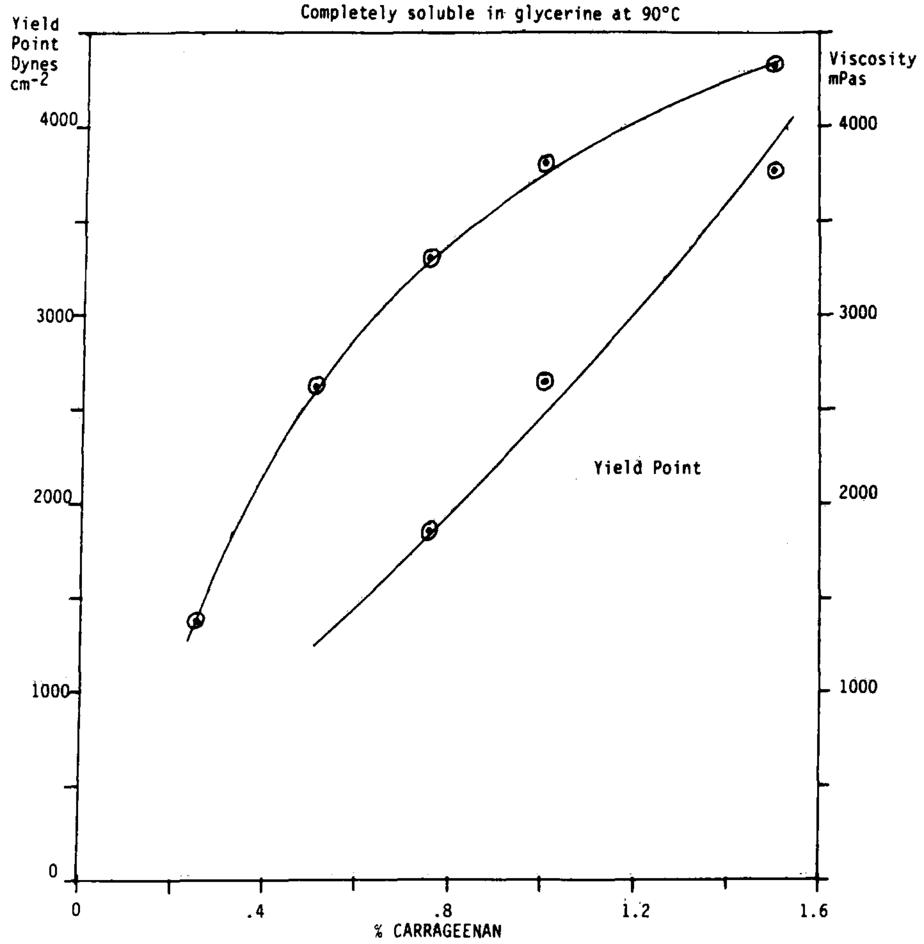

Fig. 9. Sodium iota carrageenan in anhydrous glycerine, yield point and apparent viscosity (at 85·1 s^{-1}). (Using a Fann rotating cylinder Viscometer at 25°C.)

to gel. Gelation can be brought about by cooling below the sol–gel transition, adding gelling ions or adding to propan-2-ol.

The physics behind the ionic gelation is very well understood and its application to entrapment is summarized in Fig. 13. In the absence of added salts, a kappa carrageenan such as Gelcarin™ GP 911 from FMC Corporation's Marine Colloids Division is soluble just below 60°C with a sol–gel transition on cooling at around 25°C. In the presence of K^+, however, the sol–gel transition on cooling moves to higher temperatures. Thus the species to be trapped should be dispersed, emulsified or dissolved in the carrageenan solution which is then cooled to just above its sol–gel transition and then dropped, injected or sprayed into potassium chloride solution or solutions of other gelling ions. The system

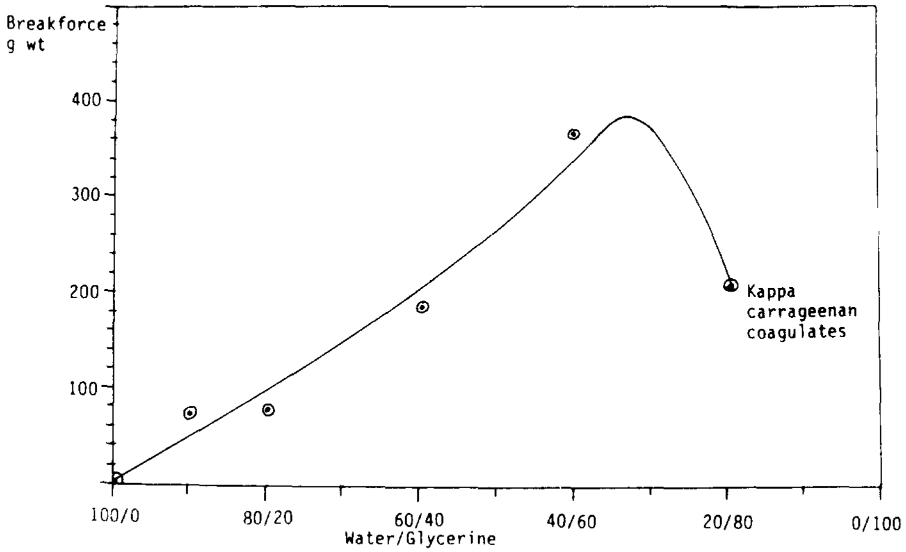

Fig. 10. Gel break force of a kappa carrageenan dissolved in water/glycerine (0·5% on continuous phase). Performed on Instron testing equipment using a large plunger with a descent rate of 50 mm/min at 25°C.

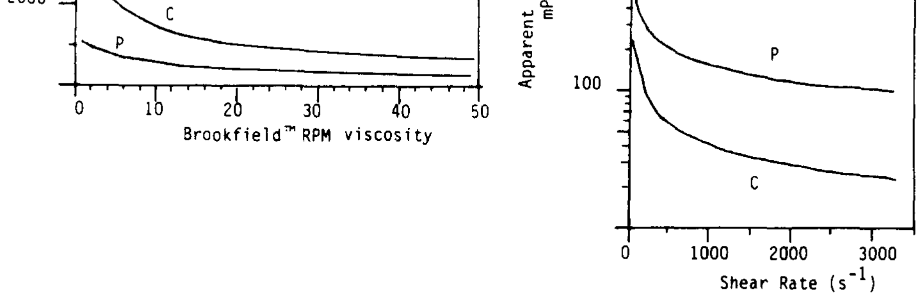

Fig. 11. Aircraft de-icers. Shear thinning profiles for Type II (thickened) fluids. C, carrageenan thickened fluid (1/4% Gelcarin GP 379); P, prior art fluid (Hoechst 1704). Gelcarin GP 379 is a trade name for a gelling carrageenan. Hoechst 1704 is a trade name of Hoechst AG.

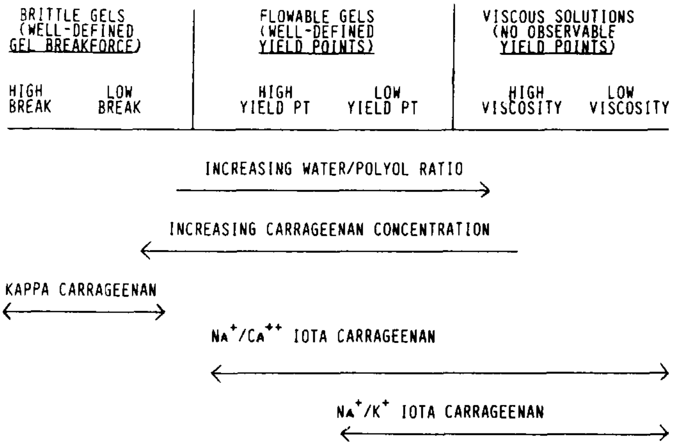

Fig. 12. Texture profile for carrageenan in water/polyols.

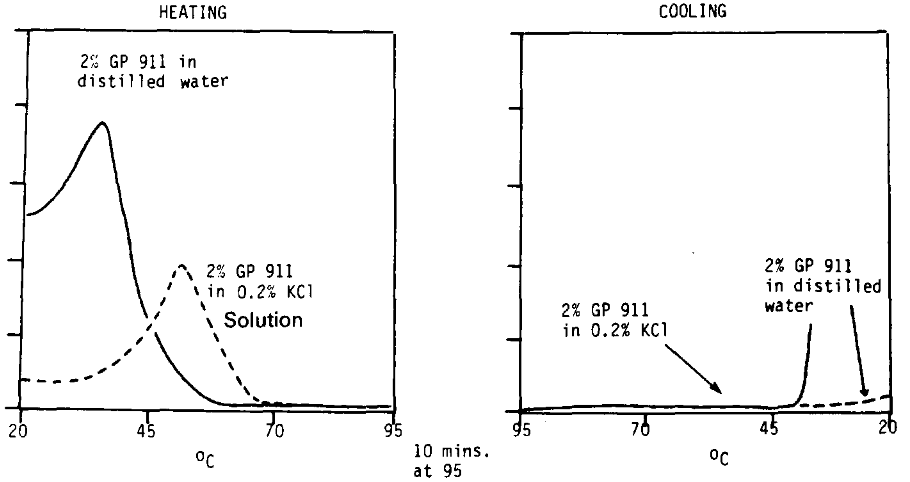

Fig. 13. Entrapment hydration and gelation characteristics of Gelcarin GP 911. In the absence of K^+, 2% Gelcarin GP 911 has a sol–gel transition at around 25°C. Two percent Gelcarin 911 solution below 30°C will gel on contact with K^+ ions. Gelcarin GP 911 is a trade name for a gelling carrageenan.

immediately gels trapping whatever is in the aqueous phase. The beads (which contain around 98% water) can be removed by straining and dried.

When viewed microscopically, the beads, whose size depends only on the initial droplet, appear to have a carrageenan coating. Loadings as high as 2 g active ingredient to 18 g of the 2% carrageenan solution can be obtained (2 g ingredient is trapped by only 0·36 g dry carrageenan).

Obviously, at these loadings the trapped ingredient serves to support the bead. The hardness of the bead can be controlled by incorporation of small quantities of polyol into the carrageenan solution. As little as 1% PEG 600 will soften the beads and enable an increase in the loading of many active ingredients.

The dried beads may be coated in wax or another material to impart chemical resistance or added diffusion control.

Air freshener gels

Dating from the late 1960s, these are perhaps the largest non-food application for carrageenan after dentifrice. The gels are a classic example of entrapment followed by timed release. They differ from the beads described above in a number of important ways aside from size. The method of forming beads gives particles coated in carrageenan and are dried to a moisture content of around 7%. They are very effective in inhibiting flavor and fragrance oils from diffusing into the environment. Air freshener gels, on the other hand, retain their original moisture content which is lost along with the fragrance oil when the air freshener gel is exposed to the air during use. As evaporation takes place, so the gel shrinks.

Typically, air freshener gels are manufactured by dispersing the formulations, which contain carrageenan and gelling ions, into hot water heated to 85°C. The carrageenan and ionic environment are selected so that the carrageenan is soluble at this temperature with a sol–gel transition on cooling around 44°C. The vats are then cooled to around 65°C and the fragrance oils blended in before the mix is sent to the filling machines. The containers can be filled hot, paletized and allowed to cool slowly or quickly by refrigeration. If the systems are subjected to shear stress from mixing or filling around the sol–gel transition temperature, the gel structure becomes broken and the product is ruined.

HUMIDITY CONTROL

The concept of a humetically sealed package is somewhat of a misnomer since almost all commercially produced packages leak to some extent. For most purposes the loss of moisture resulting from such leakage is unimportant but there are some applications when this is not the case. When it is necessary to control the humidity within a package, a small nugget of carrageenan gel can be used. Moisture lost by leakage is replaced at the expense of the gel which merely shrinks in size. The vapor pressure inside the packet is controlled by choice of carrageenan and ionic environment which in turn controls the viscoelasticity of the gel and its water retention properties. The addition of polyols greatly influences water loss from a carrageenan gel.

DRUG DELIVERY SYSTEMS

Many pharmacologically active ingredients are destroyed in the stomach or gastrointestinal tract but can be safely absorbed through the buccal linings (for example, isoprenaline sulfate, an adrenaline-like compound). The problem is to maintain the drug in the mouth long enough for absorption to take place, which is exacerbated if the drug has a bad taste. There is a considerable body of patent literature on the use of gums, carrageenan in particular, for entrapping the active ingredients in a hydrocolloid matrix to give a delivery system which will release the active ingredient in a prolonged and controlled fashion when incorporated into a variety of vehicles such as chewing gums (Yang & Sharma, 1986).

If the trapped material is tabletized, the technique can be used to administer drugs orally which would taste too bad to be given dispersed in conventional vehicles. This is particularly important for children or geriatric patients.

CELL IMMOBILIZATION

The area of immobilized cells and organelles has expanded very fast. Many new techniques for the preparation of immobilized cells have been developed during the past decade and a broad spectrum of applications has been investigated. Increasingly more gentle immobilization procedures have evolved to the point when it now seems possible to hold any cell structure and keep it alive and viable (Mattiasson, 1983).

In 1977 Chibata *et al.* discussed extensively the use of carrageenan for the trapping of microorganisms and enzymes in the presence of ammonium ion, a metal ion, a water-soluble amine or a water-miscible organic solvent. The immobilized enzyme or microorganism thus obtained showed a high level of catalytic activity for a long period of time and could be used for continuous enzymatic reaction with substrates. In a more recent review article, Mattiasson lists no less than 16 separate references to the entrapment of cells in carrageenan. The techniques are essentially the same as those used for entrapping dispersed pigments or other materials described above. A recent article on immobilized enzymes/cells in organic synthesis (Gaucher & Behie, 1987) discusses the factors affecting the choice of carrageenan, bead-casting protocols and apparatus and gel hardening — all of which affect bead survival under physical stress and cell growth within the gel matrix. One of the chief advantages of carrageenan over other gel-matrix-forming polymers is the mild conditions under which gels form with carrageenan. Enzyme activity of immobilized cells entrapped in carrageenan is generally high and stable and in addition the cell matrix is readily converted to a cell suspension (Wada *et al.*, 1979).

The development of immobilized cell technology has required several new analytical techniques for comparing cell processes in gel matrices with those of free cells (Freeman *et al.*, 1982). Some of the methods used for free cells cannot be directly applied to entrapped cells because the matrix often interferes with the assay (Jones *et al.* (1984).

The applications for cell immobilization techniques are varied in the extreme and can range from ethanol production as a potential source of liquid fuel (Chibata, 1979; Jain *et al.*, 1985) to the prolonged survival of transplanted islets of Langerhans encapsulated in biocompatible membranes (O'Shea *et al.*, 1984). Two recent books (Rosevear *et al.*, 1987; Tampion & Tampion, 1987) review the published methods of immobilization giving much needed guidance to the research worker on the choice of a suitable method.

Industrial research on immobilized enzymes has fallen back from a peak because it failed to address fully the key issue, which is that many enzymes are still not sufficiently stable for practical application even when immobilized (Dunhill, 1988).

BREWING INDUSTRY

Kappa carrageenan functions to precipitate protein materials and iota carrageenan provides binding action to allow easier removal of the precipitates during the clarification stages of beer production. These properties are now extensively used by brewers to remove colloidal materials (Siebel & Sons Co., 1988).

OIL WELL COMPLETION FLUIDS

To avoid damage to the production stratum, clear water fluids as distinguished from drilling muds are used on completion and reworking operations as a standard oil well drilling practice. The clear water fluids are concentrated water solutions of common metal salts, such as NaCl, $CaCl_2$, $CaBr_2$, $ZnBr_2$, and so on. The salt selected and concentration employed are determined by the desired density of the fluid. To obtain very high densities, zinc salts such as $ZnBr_2$ and mixtures with $CaBr_2$ are used.

Additives are used with clear water fluids to control and increase their viscosity. Increased viscosity enhances the carrying capacity of the fluid, reduces fluid loss and tends to promote conditioning of the formation to minimize caving and water damage to water-sensitive formations. Polysaccharide gums are commonly employed for this purpose (Chatterji & Borchardt, 1980). It has been found that under certain conditions carrageenan viscosifiers give greater viscosity effects at the same additive level than hydroxyethylcellulose (HEC), a commonly used polymer for completion fluids (Mosier *et al.*, 1982, 1983).

Work at Marine Colloids has shown that carrageenan can viscosify certain high-density completion brines and maintain a predictable viscosity over the wide temperature ranges encountered during drilling completion operations. A problem with HEC is that the polymer can come out of solution at different temperatures depending on the brine density (Shelso, 1988).

PAPER AND TEXTILE INDUSTRIES

Marbling is probably one of the oldest techniques used for decorating, perhaps originating in the 15th century to prevent the forging of legal documents. In Turkish marbling, water-based inks or pigments are floated on a gelatinous surface and then moved around with picks and combs until a desired pattern is achieved. Mordanted paper or fabric is laid on the surface of the solution to absorb the color and is then lifted away (London, 1987).

The gelatinous surface is made using a cold-water-swelling carrageenan powder sprinkled into water and mechanically dispersed. The inks, if added at the correct viscosity (which must be determined by trial and error), adhere to the soft swollen gel particles and float to the surface of the bath.

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