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FMC BioPolymer

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FMC Alginates

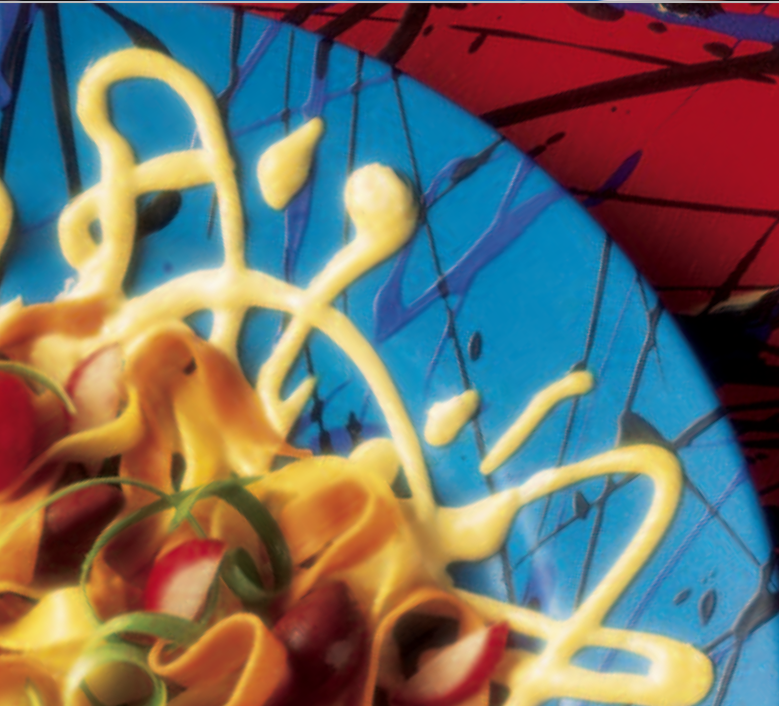
General Technology

- DARILOID[®]
- KELCOLOID[®]
- KELCOSOL[®]
- KELSET[®]
- KELTONE[®]
- LACTICOL[™]
- MANUCOL[®]
- MANUGEL[®]
- PROTANAL[®]
- PROFOAM[™]
- TEXTUREZE[®]

- LAMITEX[®]
- PROTAWELD[®]
- SCOGIN[®]

FMC BioPolymer

Know how. It works.SM



Know how. It works.SM

With over 60 years of experience in the development and production of alginate products, FMC BioPolymer is well prepared to serve you as a resourceful and reliable partner.

Working with a broad palette of alginates and an even broader range of problem-solving skills, our know-how can help you add structure, texture and stability to achieve optimum results.

Our high quality alginates are manufactured under the stringent requirements of ISO 9001 certification – which applies not only to production but also to R&D, storage and shipping.

And the customer service we provide, both before and after the sale, adds great value to our alginates. You can rely on us for the sound advice and formulation and processing problem-solving that can help you reach new levels of efficiency in your operation. You can also count on FMC BioPolymer to help turn your innovative thinking into practical, profitable reality.

FMC BioPolymer. Adding structure, texture and stability– naturally.

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An Introduction to Alginates

Alginate is classified as a hydrocolloid (a water-soluble biopolymer of colloidal nature when hydrated). The first scientific studies on the extraction of alginates from brown seaweed were made by the British chemist E.C. Stanford at the end of the 19th century, and the large-scale production of alginate was introduced 50 years later.

Alginate is one of the most versatile biopolymers and is used in a wide range of food, pharmaceutical and specialty applications for:

- Thickening
- Stabilizing
- Gelling
- Film forming

Today, FMC BioPolymer is among the world's largest alginate manufacturers. Together with our carrageenan and cellulose gel (microcrystalline cellulose) we offer a full range of functionalities and capabilities to assist formulators in creating and launching innovative products and systems, including:

- Cold soluble
- Cold setting
- Heat stable
- Freeze/thaw stable

Origins of Alginates

The primary brown seaweed utilized by FMC BioPolymer for the extraction of alginates is *Laminaria hyperborea*. This type of seaweed is harvested along the West Coast of Norway, where the sustainable, renewable crop grows naturally in the clean Arctic waters. The plants are harvested in fairly shallow waters, at depths of 2-15 meters. Special trawlers have been developed to harvest this seaweed, and FMC BioPolymer is the only alginate producer in the world that harvests *Laminaria hyperborea* mechanically.

Mechanical harvesting, along with careful monitoring of the resources, ensures regular long-term cropping of defined areas. FMC's yearly harvest is less than 5% of the total yearly regrowth volume of *L. Hyperborea* seaweed along the Norwegian coast. FMC has a secure raw material supply, with no risk of shortage.

In order to secure a flexible and continuous supply of raw material, which enables FMC to meet the highest demands in terms of alginate functionality, FMC also utilizes other sources of brown seaweed, harvested off the coast of Chile (see **Figure 1**).

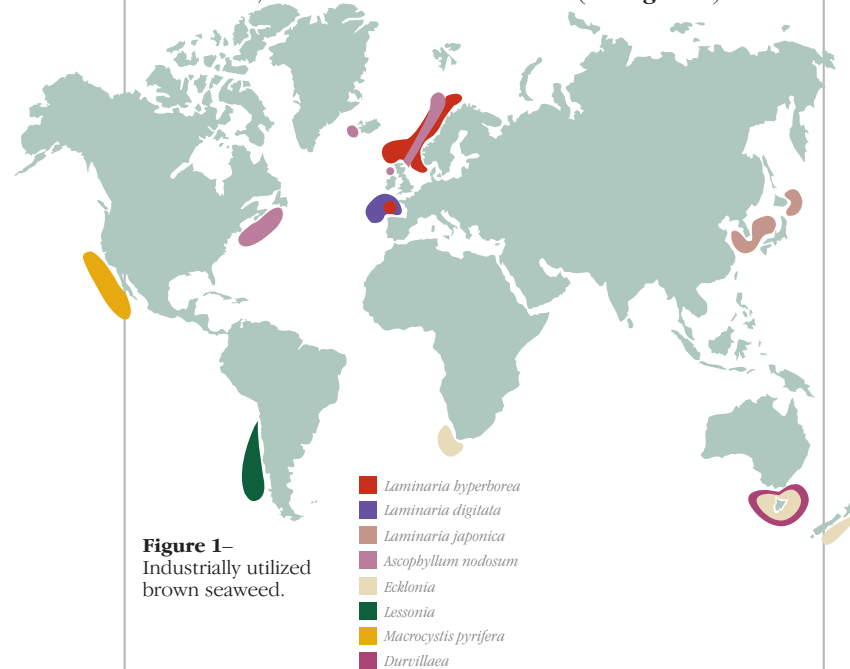
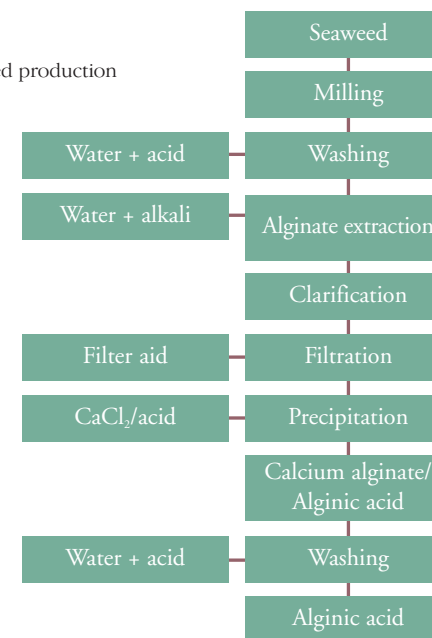


Figure 1– Industrially utilized brown seaweed.

Processing Alginates

Alginate occurs in the seaweed as a mix of calcium, magnesium, sodium and potassium salts. More than 20 stages of controlled processing are required in order to obtain high quality alginates that offer the exceptional functionality of FMC's branded alginates.

Figure 2– Simplified production of alginic acid.



FMC BioPolymer manufactures more than 200 grades of alginates – alginic acid and its sodium, potassium, ammonium, magnesium and calcium salts. Sodium, potassium, ammonium, magnesium alginates and PGA are water soluble. Alginic acid and calcium alginate swell in water. In addition, FMC BioPolymer offers different grades of esterified alginate in the form of propylene glycol alginate (PGA).

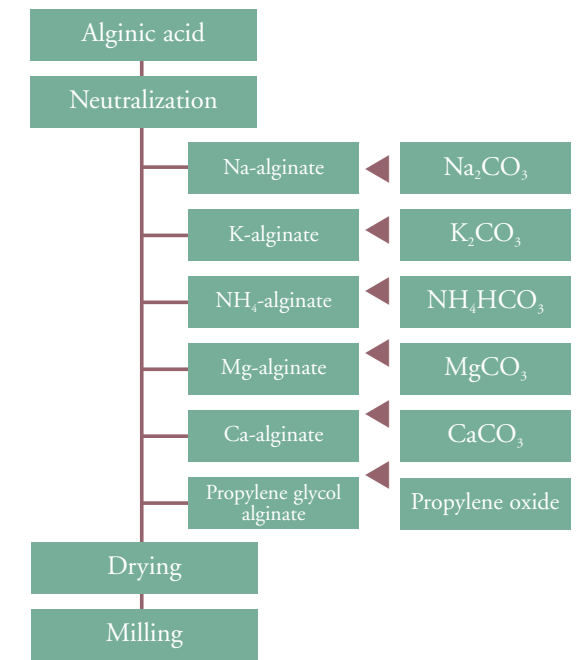


Figure 3– Commercial salts and ester produced from alginic acid supplied by FMC BioPolymer.

Chemistry

Alginate is a polysaccharide, like starch and cellulose. It is composed of several building units (typically 100–3000) linked together in a flexible chain. Long molecules constructed from identical or nearly identical building units are called polymers, while the building units themselves are called monomers. Polymers of natural origin are commonly called biopolymers.

Alginic acid is a copolymer of two uronic acids, mannuronic and guluronic acid. When producing alginates, the uronic acid is converted into the salt forms mannuronate (M) and guluronate (G) through a neutralization step (see **Figure 4**).

The G- and M- units are joined together in one of three blocks: GG..., MM..., and MG.... These are illustrated in **Figure 5**. The proportion, distribution, and length of these blocks determine the chemical and physical properties of the alginate molecules. While G-blocks provide gel-forming potential, MM and MG units provide flexibility to the uronic acid chains.

The chemical composition of alginate varies according to seaweed species and even within different parts of the same plant. As with all products produced from a natural resource, alginate properties are subject to seasonal variations. By selecting raw materials with varying but known properties, FMC BioPolymer has the experience to manufacture alginates with consistent quality and properties in a wide range of grades.

Figure 4– The monomers of alginate

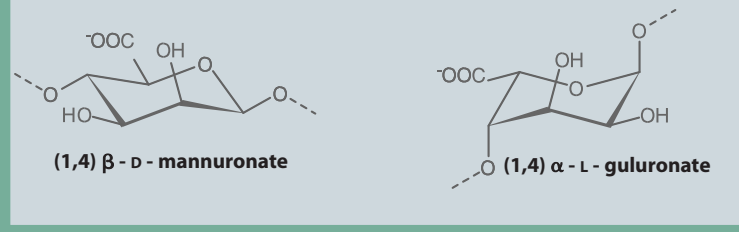
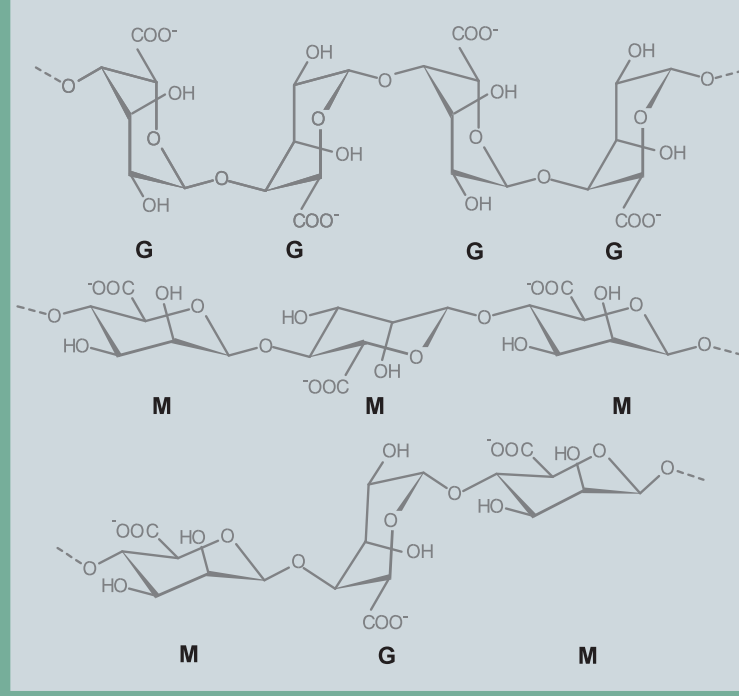


Figure 5– Alginate block types



Functionality and Rheology

Years of experience has provided us with the expertise to carefully select and process our resources resulting in controlled properties such as viscosity and gelation.

Viscosity– Through selection of grade and formulation, the flow characteristics of alginates can be controlled; from free-flowing (low viscosity) to drip-free (high viscosity). Alginates must be

fully hydrated to obtain optimum functionality. The aqueous solutions of alginates have shear-thinning characteristics, i.e., the viscosity decreases with increasing shear rate. This property, illustrated in **Figure 6**, is also called pseudo-plasticity, or non-Newtonian flow.

The viscosity of an aqueous solution of alginate depends on the concentration of alginate and the length of the alginate molecules, i.e., the number of monomer units in the chains. The longer the chains the higher the viscosity at similar concentrations (see **Figure 7**).

Figure 6– Viscosity as a function of shear rate

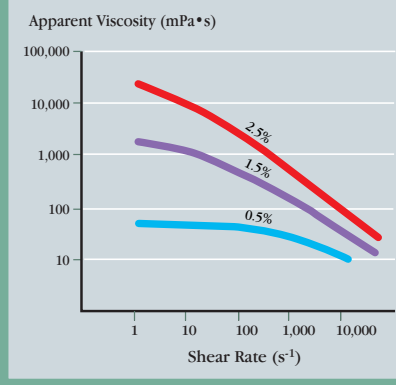
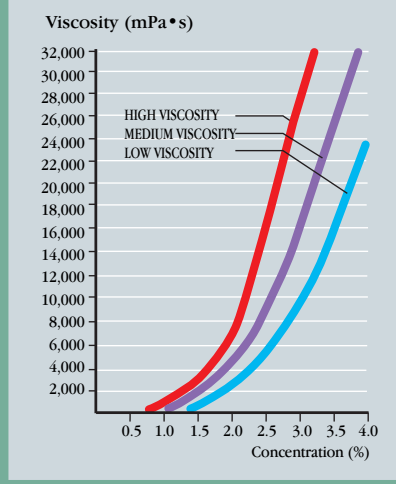


Figure 7– Viscosity as a function of concentration of Protanal® alginate



On dissolving alginates in water, the molecules hydrate and the solution gains viscosity. The dissolved molecules are not completely flexible; rotation around the glycosidic linkages in the G-block regions is somewhat hindered, resulting in a stiffening of the chain.

Solutions of stiff macromolecules are highly viscous. Temperature defines the energetic state of any chemical molecule. Hence tempera-

ture influences the response of alginates to shear forces. Increasing temperatures will result in a decrease in viscosity. As a general rule, temperature increases of 1°C lead to a viscosity drop of approximately 2.5% (see **Figure 8**).

Acid Conditions– Standard grades of alginate will precipitate or form gels in acidic conditions. The pK_a values for mannuronic and guluronic acid are 3.38 and 3.65, respectively. To increase the stability of an alginate to acid, the alginate may be converted to propylene glycol alginate (PGA) which is soluble in acid. This is achieved by reacting the free carboxylic group of the alginic acid with propylene oxide (see **Figure 9**).

Figure 8– Viscosity of three 1% Protanal alginate solutions at different temperatures

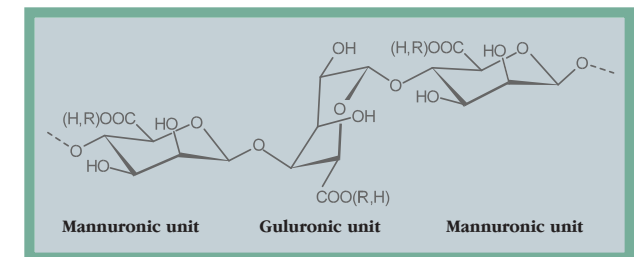
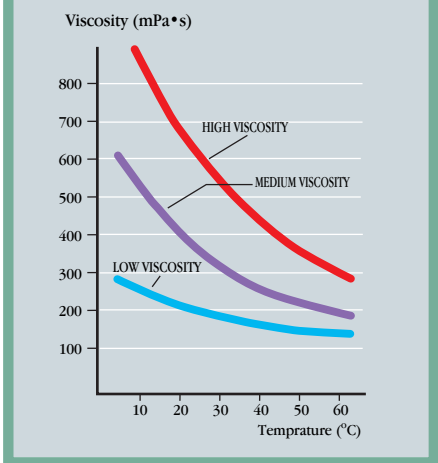


Figure 9– Propylene glycol alginate: alginic acid chain with some acid residues esterified (R indicates ester group; H indicates acid group).

Gelation

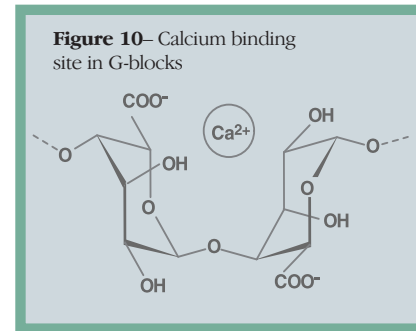
As previously mentioned, alginates contain various proportions of mannuronate and guluronate monomers.

To form a gel, alginates must contain a sufficient level of guluronate monomers in a block to react with calcium. The reactivity with calcium and the consequent gelling capacity is a direct function of the average length of the G-blocks. The alginate containing the highest level of GG fractions, produced from the stems of *Laminaria hyperborea*, possess the highest ability to form strong gels (see **Table 1**). FMC BioPolymer responsibly manages these resources to solidify our position as the leading and long-term supplier of alginate for applications that require these superior gel-forming capabilities.

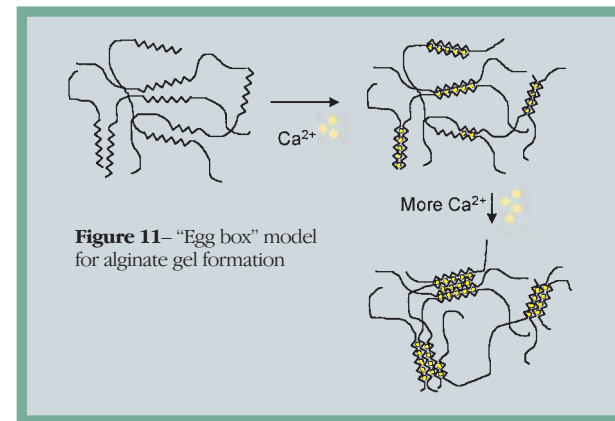
Table 1
Typical M- and G- block profiles for different seaweeds as measured by nuclear magnetic resonance spectroscopy (NMR).

Type of Seaweed	%MM	%MG & GM	%GG
<i>Laminaria hyperborea</i> (stem)	17	26	57
<i>Laminaria hyperborea</i> (leaf)	36	38	26
<i>Lessonia nigrescens</i>	40	38	22
<i>Lessonia trabeculata</i>	25	26	49
<i>Durvillaea antarctica</i>	56	26	18
<i>Laminaria digitata</i>	43	32	25
<i>Eclonia maxima</i>	38	34	28
<i>Macrocystis pyrifera</i>	38	46	16
<i>Ascophyllum nodosum</i>	44	40	16
<i>Laminaria japonica</i>	48	36	16

The Chemistry of Gelation- Regions of guluronate monomers, G-blocks, in one alginate molecule can be linked to a similar region in another alginate molecule by means of calcium ions or other multivalent cations (see **Figure 10**).



The divalent calcium cation, Ca^{2+} , fits into the guluronate block structure like eggs in an egg box (see **Figure 11**). This binds the alginate polymers together by forming junction zones, resulting in the gelation of the solution.

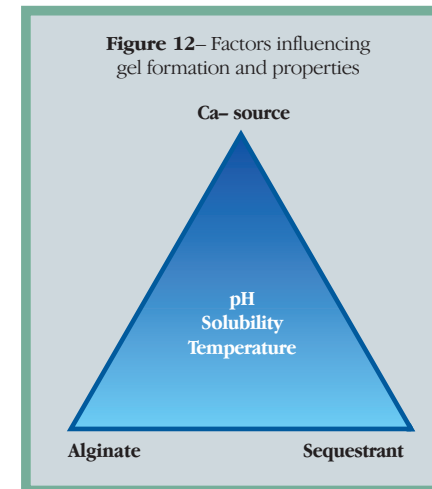


An alginate gel may be considered to be partly in a solid and partly in a solution state, the junction zones representing the solid state. After gelation the water molecules are physically entrapped within the alginate matrix, but are still free to migrate by diffusion. The water-holding capacity of the gel is due to capillary forces.

Alginates are cold soluble in water and develop into gels when exposed to calcium ions. They do not require a heating and cooling process to form a gel, as is the case with most gelling agents. By adjusting formulations, alginate gels offer a range of structures, from firm and brittle to soft and pliable. To assure optimum gelling properties it is essential that the alginate is in a fully hydrated state and is homogeneously distributed in the final product. There are three basic components in forming a typical alginate gel:

- Alginate
- Calcium Salt
- Sequestrant

Alginate, calcium and the sequestering agent control the gelling system structure and the rate at



which the gel forms. The grade of FMC alginate, calcium source and sequestering agents must be matched with the manufacturer's process and recipe or formulation to reproduce the desired properties in the final product (see **Figure 12**).

The uniqueness of alginates as gel formers is their ability to form heat-stable gels that can develop at room temperature. This is of particular importance when alginates are used as gelling agents in restructured products such as onion rings and bakery fillings, which may be subjected to further heat processing.

Forming a Gel

Several gelling systems based on alginates can be formulated, but the most frequently used are diffusion setting or internal setting.

Diffusion setting, neutral pH- In a diffusion setting system at neutral pH, an alginate solution, or an alginate containing mixture, is gelled by being dipped into, or sprayed with, a calcium salt solution. Calcium chloride is used most often. The calcium ions diffuse into the alginate solution and react with the alginate molecules to form a calcium alginate gel.

This process is especially suitable for relatively thin or small dimension materials, such as pimiento strips and onion rings, or to provide a thin coating on a product surface. The diffusion process can be increased by raising the concentration of calcium in the setting bath or spray and by using a strongly calcium-reactive alginate, such as an alginate with a high proportion of G-blocks.

Diffusion setting, acid pH- The diffusion setting system can also be used to form a gel in a low or acid pH. In this system, a calcium salt which is insoluble at neutral pH, is mixed with the alginate. When the acid comes into contact with the surface of the mass, the calcium salt is solubilized. The soluble calcium will then react with the alginate and start the gelation process as acid diffuses into the alginate containing material.

Internal setting, neutral and acid pH- In an internal setting process, calcium is released within the product under controlled conditions. This process employs the combination of alginate, a slowly soluble calcium salt and a suitable calcium sequestrant, such as a phosphate or citrate. The sequestrant is needed to bind free calcium and prevent pregelation of the alginate during the time the product is mixed, and before it is cast into a

desired shape. The shorter the mixing time, the lower the level of sequestrant needed.

The internal setting process may be performed at neutral or acidic pH. The acidity may be obtained by the addition of an acidifier, which will accelerate the solubility of calcium salts.

Setting after heat treatment– In this process the alginate is dissolved in water together with calcium salt and a sequestrant, and kept hot. The high temperature counteracts gelation because the alginate chains are in flux due to thermal motion, which prevents them from associating. Setting begins when the solution begins to cool. When cooled, the calcium alginate reaction will form a heat stable gel. Relatively soft gels can be formed at 0–50°C under these conditions.

Alginate/Pectin Gels– High-methoxy pectins are only able to form gels at high sugar solids levels within a narrow pH range. When a sodium alginate is included, gel formation takes place at low solids and below pH 3.8; the gel is reversible, a property used commercially in nappage and jelly topping. The alginate-pectin synergism is one of very few interactions for alginate with other hydrocolloids.

Film forming capabilities– When a thin layer of alginate gel or solution is dried, a film or coating is formed. The unique film-forming capabilities of alginate offer formulators opportunities to develop innovative products and delivery systems. Protanal® alginate offers excellent transparency and can be either soluble or insoluble. Soluble films of sodium alginate are made by casting and drying, while insoluble or gelled alginate films are produced by applying a layer of alginate solution followed by cross-linking with calcium salt and then drying.

Preparing Alginate Solutions and Gels

Mixing and Dissolving– When dissolving alginate, it is crucial that the water is vigorously being stirred in order to create a vortex. Alginate should be added slowly into the vortex of the water to avoid lumping and stirred until completely hydrated, typically 5-30 minutes depending on the grade of Protanal® alginate and the processing equipment. Premixing alginate with a powder, such as sugar, or with a water-miscible liquid, such as alcohol or glycerol, will facilitate dispersion and subsequent dissolution.

Although alginates are generally less susceptible to microbial attack than many other carbohydrates, preservatives are recommended for use in systems with high moisture content. A suitable preservative such as sorbic acid, potassium sorbate, benzoic acid, sodium benzoate or esters of hydroxybenzoic acid is recommended for food applications. In industrial applications formaldehyde, sodium pentachlorophenate and other phenolic derivatives may be used.

Under neutral conditions alginate systems are stable at room temperature. As with most carbohydrates, alginates are susceptible to hydrolysis or degradation in acid and alkali, especially at high temperatures for extended periods. To limit the effect of heat and acid it is recommended that high heat be applied for a short period of time, and only if necessary.

Main Applications, Functions and Benefits

FOOD

Application	Type of Alginate	Functions and Benefits
Bakery Cream and Filling	Protanal®	<ul style="list-style-type: none"> Instant gelling and thickening; heat stability; range of different textures; good mouthfeel and flavor release
Beer	Profoam™	<ul style="list-style-type: none"> Improves and maintains foam levels
Dressing	Kelcoloid®, Protanal ester	<ul style="list-style-type: none"> Thickening, stabilizing, emulsifying; good mouthfeel; acid stable
Fruit Juice	Kelcoloid, Protanal ester	<ul style="list-style-type: none"> Stabilizing, emulsifying
Fruit Filling and Preparation	Protanal, Manucol®, Manugel®	<ul style="list-style-type: none"> Gelling, thickening, stabilizing; prevents syneresis; excellent heat stability; cold and hot process; wide range of textures; available for low to high brix systems
Dry Mix Dairy	Alginade®, Dariloid®	
Ice Cream and Sorbet	Protanal	<ul style="list-style-type: none"> Stabilizing; controls viscosity; prevents crystal formation and shrinkage; contributes to even and slow meltdown
Low Fat Spread	Protanal, Kelvis®	<ul style="list-style-type: none"> Stabilizing; good mouthfeel, texture and flavor release
Meat	Protanal, Textureze®	
Petfood	Protanal, Textureze	<ul style="list-style-type: none"> Gelling; produces heat-resistant and retortable, meat-like chunks
Restructured Food	Protanal	<ul style="list-style-type: none"> Excellent gelling ability; heat stability; easy to form
Yogurt	Manugel	<ul style="list-style-type: none"> Stabilizing; good mouthfeel, texture and flavor release

SPECIALTY

Application	Type of Alginate	Functions and Benefits
Textile Printing	Lamitex®, Scogin®	<ul style="list-style-type: none"> Gives the desired rheology to print pastes; is inert to dyes and fibers; has excellent wash-out properties; is extremely pure
Paper	Scogin®	<ul style="list-style-type: none"> Enhance greaseproof properties, oil resistance, and solvent holdout; improves rheology, water-retention, runability, ink holdout, and printability
Welding	Protaweld™	<ul style="list-style-type: none"> Lubricant stabilizer and “green strength” agent in the extrusion of high quality welding rods

