KIMICA

English

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Marine **Biopolymers**

Alginate

KIMICA INTERNATIONAL

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2019.8

KIMICA Corporation (KIMICA) is a manufacturer and world-wide supplier of "alginate", (alginic acid and its derivatives), which is a natural polysaccharide. Alginates are extracted from brown algae, which are in abundant supply in the oceans.

In 1941 KIMICA became the first company in Asia to successfully produce alginates on a commercial scale. Since then KIMICA has emerged as a global market leader in alginate manufacturing and sales.
Continuous upgrading of manufacturing technology helps assure that KIMICA Alginates remain the best in the world.

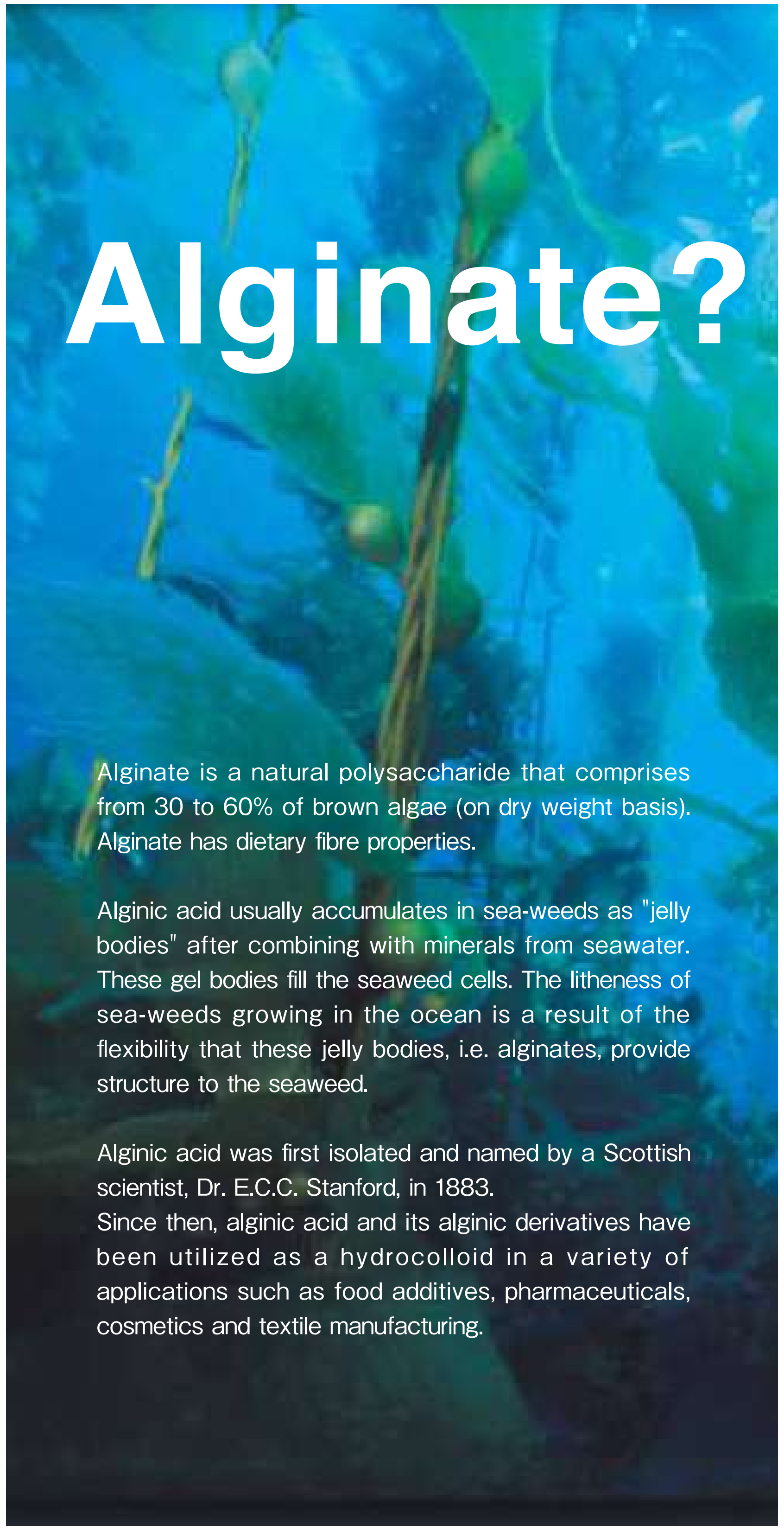
In 1988, due to extensive sales growth, KIMICA expanded by building a second manufacturing plant, KIMICA Chile Ltda. Chile was selected as the site because the long coastline of Chile has abundant supplies of the finest alginate containing seaweeds. Today, the KIMICA plants in Japan and Chile each produce the full spectrum of alginate products, which are then sold throughout the world.

Our R&D staff consists of seaweed industry experts from several disciplines, (physical sciences, engineering, pharmaceutical and agricultural backgrounds), who are devoted to the technical advancement of alginate production in order to respond effectively to demands from the market place.

KIMICA is happy to supply alginate products in any quantity, KIMICA will also provide customers with technical service or cooperation by making available its state-of-the-art equipment, proprietary licenses and its own expertise.

KIMICA

c o n t e n t s



Alginate?

Alginate is a natural polysaccharide that comprises from 30 to 60% of brown algae (on dry weight basis). Alginate has dietary fibre properties.

Alginic acid usually accumulates in sea-weeds as "jelly bodies" after combining with minerals from seawater. These gel bodies fill the seaweed cells. The litheness of sea-weeds growing in the ocean is a result of the flexibility that these jelly bodies, i.e. alginates, provide structure to the seaweed.

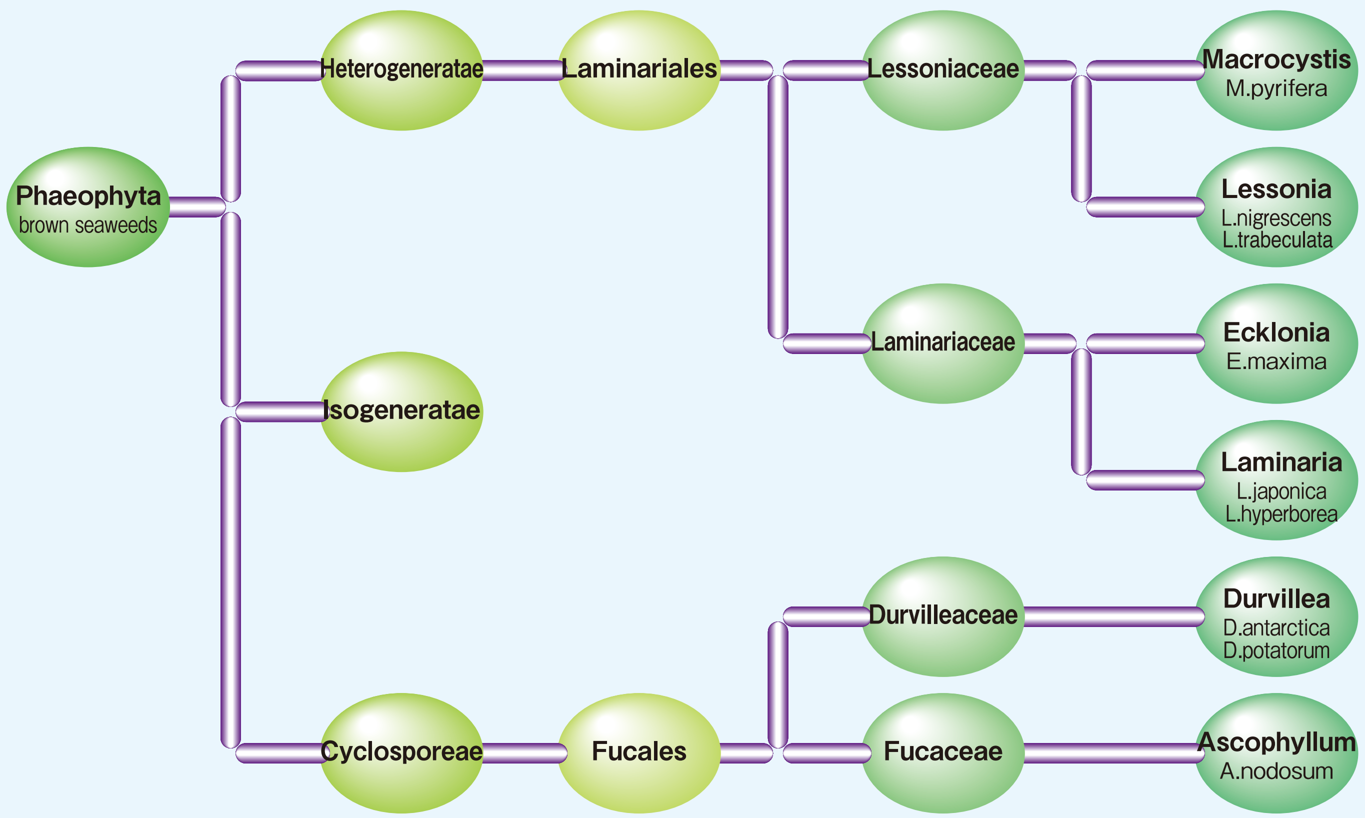
Alginic acid was first isolated and named by a Scottish scientist, Dr. E.C.C. Stanford, in 1883.
Since then, alginic acid and its alginic derivatives have been utilized as a hydrocolloid in a variety of applications such as food additives, pharmaceuticals, cosmetics and textile manufacturing.

Botany of Alginate Containing Seaweeds

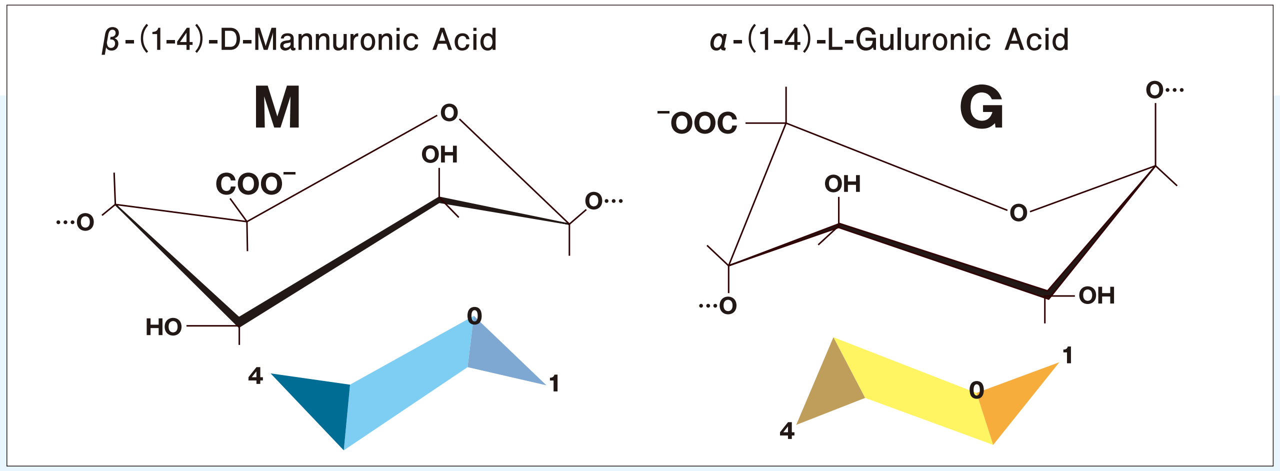
Seaweeds grow abundantly in the oceans world-wide and there are numerous brown seaweeds, the raw materials for alginate. Use of this "marine biopolymer" is attracting increasing attention as time progresses.

KIMICA has organized a world-wide network for the optimal collection of several species of seaweeds suitable for industrial mass production. This makes it possible to produce a diverse array of stable alginate products in a timely manner for all our global customers.

Botanical classification of the brown seaweeds, the raw materials of alginates:

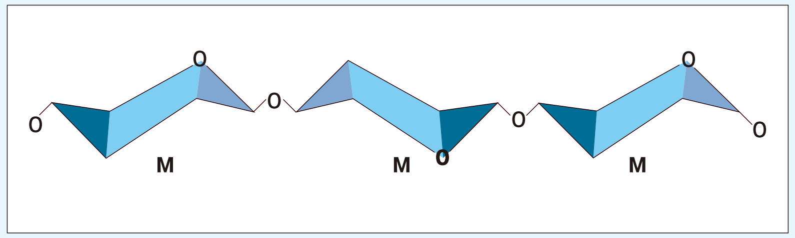


Chemical Structure

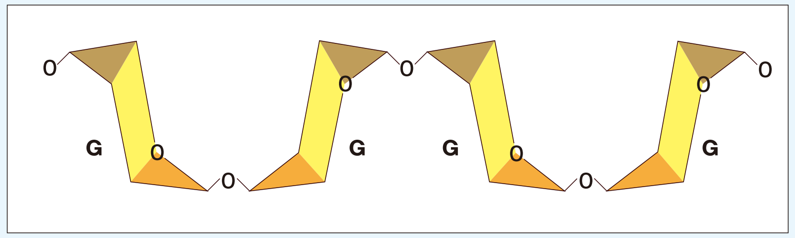


Alginic acid, a Polysaccharide is composed of two types of Uronic acid: Mannuronic acid unit (M) and Guluronic acid unit (G), which form three kinds of polymer segments of blocks:

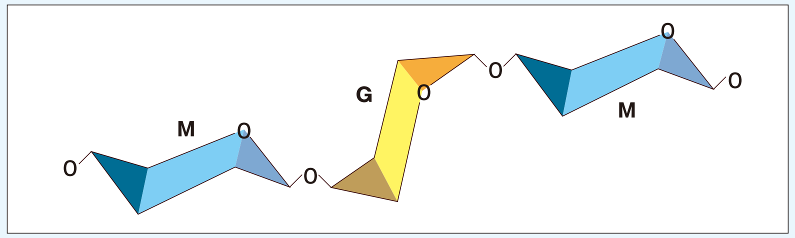
M blocks : comprised only of M-M bonding,



G blocks : comprised only of G-G bonding,



M&G random blocks : comprised of M-G random bonding,



Differences in M/G ratio and block configuration account for the differences in alginate properties and functionality, especially in gelling capability and gel strength. The M/G ratio is dependent upon such factors as the species of seaweed, the part of the seaweed used, the harvest location, and the harvest season.

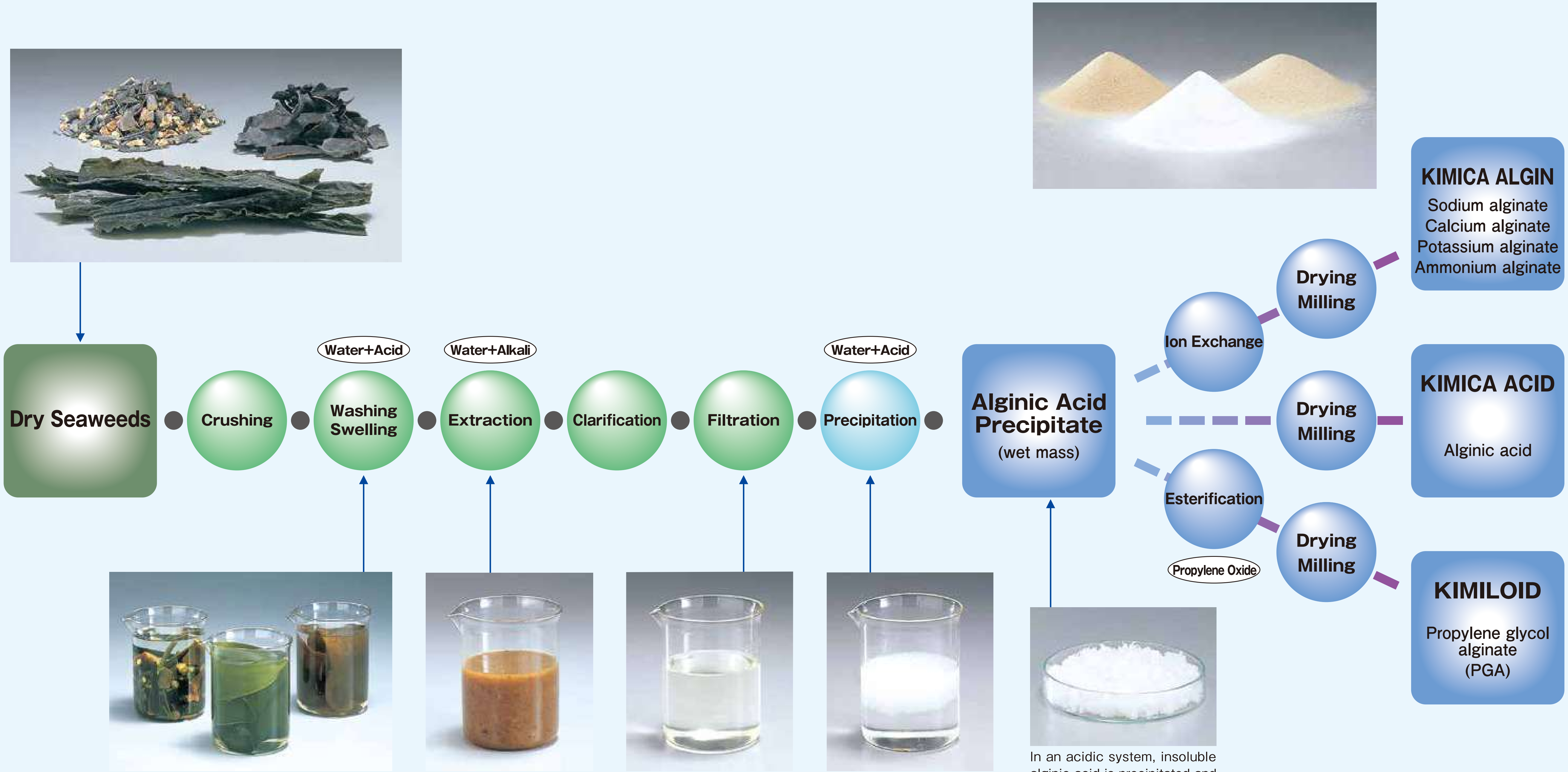
The carboxyl groups within the M and G units are easily ion-exchanged, and can react with several kinds of cations. This results in changes in alginate properties and functionality.

Utilizing these chemical reactions and the resultant changes in functionality, alginates have many commercial applications such as a thickening agent, as a gelling agent, a dispersion stabilizer, a texturizer and as a filament or film former.

Manufacturing Process

Alginic acid and its derivatives are manufactured commercially involving several operations including extraction and purification of the seaweed polysaccarides, utilizing ion-exchange reaction.

There are two methods of processing to produce alginates: the so-called "Acid precipitation method" and the "Calcium precipitation method".
KIMICA has developed and commercialized the "Acid precipitation method", from its foundation, and possesses considerable "know-how" of this production method. The "Acid precipitation method" is particularly suitable for the production of the purest alginic acid because it reduces calcium contamination. Calcium has considerable affects on the properties and functionality of the final alginic acid and its derivatives.



By reacting with divalent metal cations from seawater (such as calcium), the alginic acid in seaweed forms a water insoluble alginate gel. This alginate is partially cross-linked and retains its shape.

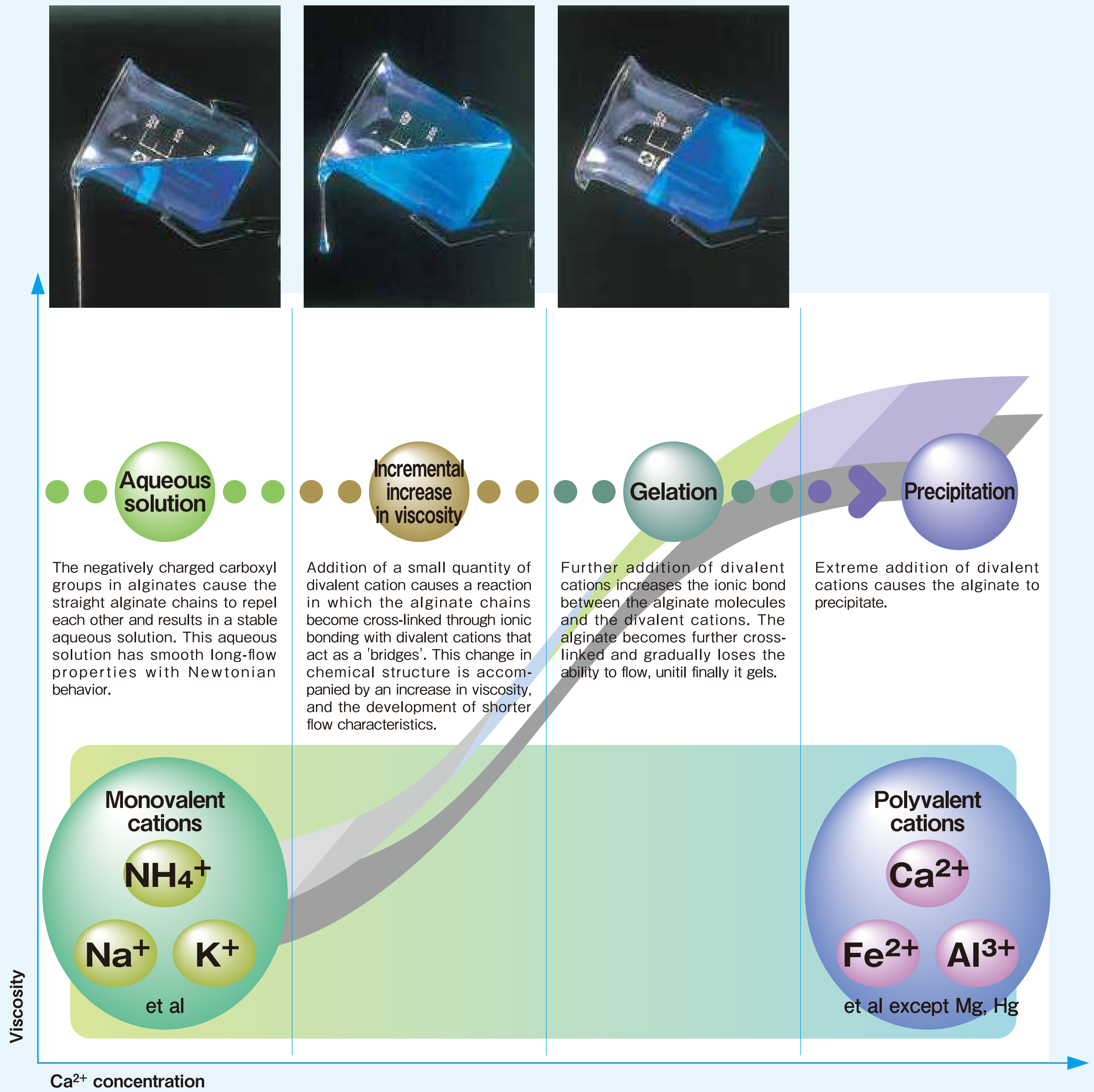
The alginate in seaweed is extracted first by conversion to water-soluble sodium alginate. The aqueous sodium alginate is then isolated by filtration from the seaweed residue.

In an acidic system, insoluble alginic acid is precipitated and isolated.

Properties of Alginates

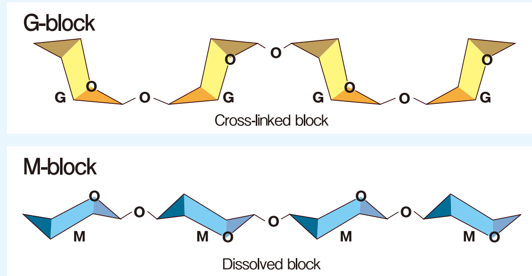
The versatility of alginate is a consequence of its behavior in aqueous solution. A variety of cations can combine with the carboxyl groups in alginate resulting in significant changes to its properties and functionality. As a result of this the performance of alginates can be "engineered".

Alginates are transformed rapidly and smoothly through ion-exchange reactions with salts of divalent metals. This is represented in the following graph that shows the viscosity change as the ion exchange between monovalent and divalent ions progresses. Initially, the solution of alginate has long flow properties. The graph shows the development of a firm gel structure as the reaction progresses. Note that magnesium alginate is water-soluble.

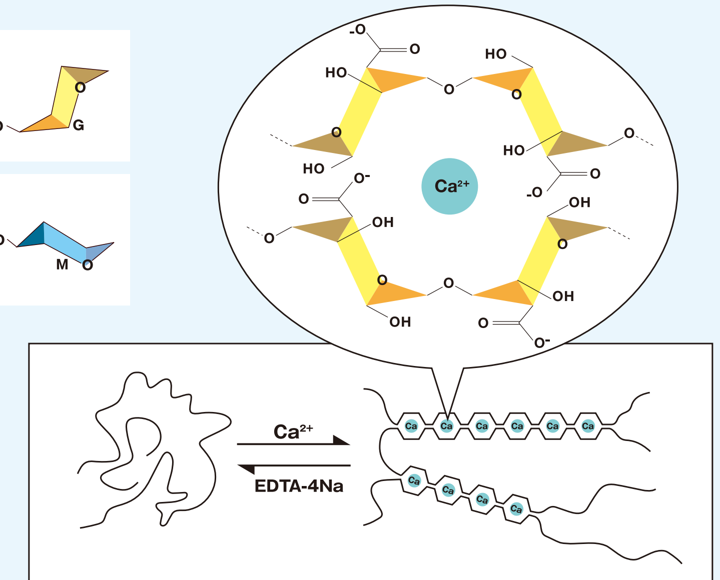


Sol-Gel Transition of Alginates

The transition from Sol (i.e. viscous fluid) to Gel (i.e. elastic body) can normally be observed visually. The gelled mass is a co-polymer of two segment types. The "cross-linked" G-block segments formed by intermolecular interaction, and the "dissolved" M-block segments.



Buckled ribbon-like G-blocks (polyguluronate segments) associate into aggregates with interstices into which the calcium ions fit, building an "Egg Box Junction" structure. These cross-links are formed by chelation of a pair of alginate polymer chains by a single calcium ion.



Sol-Gel Transition Model
Sodium Alginate vs Calcium Alginate (Egg Box Junction)

Resilient, elastic gels are obtained from M-rich alginates while firm, brittle gels are obtained from G-rich alginates. The ratio of M (Mannuronic acid) to G (Guluronic acid) is a good predictor of gel rheological properties. The stiffness of gels for fabricated products can be adjusted by blending M-rich and G-rich Alginates.

Immediate gelation occurs when calcium ions come into contact with alginate. Utilizing this, spherical gel particles can be produced by adding drops of an aqueous alginate solution into a calcium solution. Similarly, strings of gel can be produced by using a continuous stream of alginate solution.

Example : spherical gel particle production : spiking drops of a 1% aqueous alginate solution with orange colorant into a 1% calcium chloride aqueous solution.

Because an alginate gel is formed by ionic bonding between alginate and divalent/polyvalent cations, the gel is heat-stable. No breakdown occurs when this alginate gel is heat sterilized, heated in an oven, or freeze/thaw processed.

The reaction velocity of gelation between alginates and calcium ions can be controlled by adjusting the ionization velocity of calcium, as follows:

(1) Selection of calcium salt,
(2) Use of sequestrants,
(3) Changing the pH.

(For more detailed explanation of the gelation mechanism, a technical bulletin is available upon request.)

Properties of sodium alginate solution

Sodium alginate is soluble in both cold and hot water. This produces a smooth viscous solution with a neutral pH.

To make a solution

Sodium alginate has a very strong affinity for water and care is required to achieve a homogeneous solution, as follows :

(1) Add sodium alginate powder gradually to water while stirring rapidly.

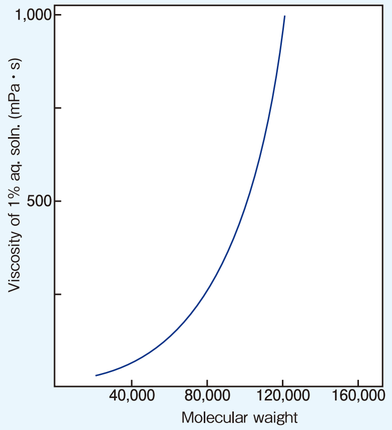
or (2) Before mixing, make a uniform mixture of sodium alginate powder with a hydrophilic powder, for example, sugar, and add the powder to water as in (1).

or (3) Before mixing, make a wet mixture of sodium alginate powder with a hydrophilic liquid, for example, alcohol or glycerin, and add the mixture to water with stirring.

Poor dispersion in water will occur if sodium alginate is added too rapidly, producing pasty, floury lumps wetted only on the outside.

Effect of M.W.

The viscosity of aqueous sodium alginate solutions is related to the molecular weight, i.e. the degree of polymerization, of the sodium alginate.

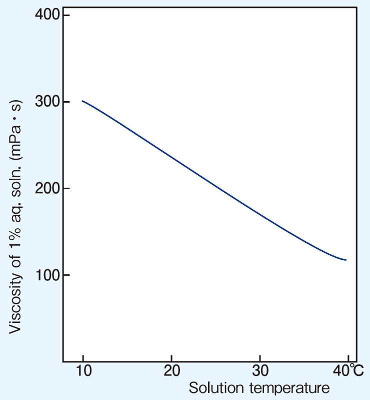


●Viscosity vs MW

Effect of Temperature

The viscosity of aqueous sodium alginate solutions decreases as the temperature increases. Temperature has little effect on freeze/thaw properties.

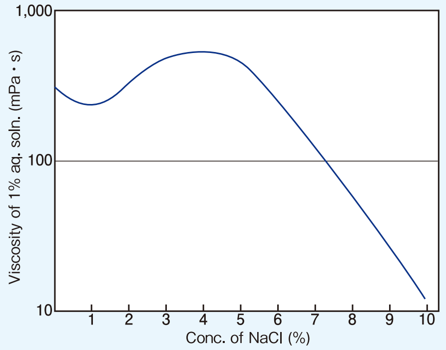
*It is necessary to pay close attention to the temperature of aqueous sodium alginate solutions. Viscosity is very sensitive to temperature.



●Viscosity vs Temperature

Effect of a monovalent electrolyte

An inorganic electrolyte such as NaCl, which provides monovalent cations, reduces the viscosity of an aqueous sodium alginate solution. This effect occurs because the monovalent cations cause the sodium alginate, a high molecular weight electrolyte, to shrink.

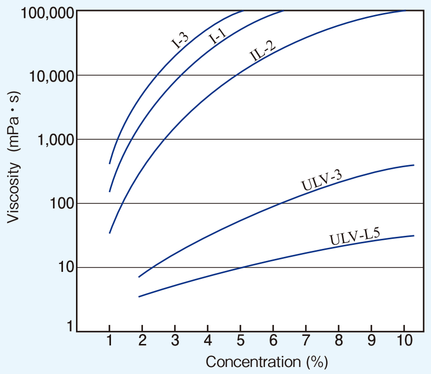


Polyvalent cations and the use of sequestrants

An aqueous sodium alginate solution reacts with polyvalent cations such as calcium ions and readily forms a gel, (see page 7). In many systems where sodium alginate is used, some calcium or other divalent ions will also be present. This is true for products ranging from dairy products to dyes. In some plants the water supply may also be high in divalent ions. An effective way to avoid undesirable effects of polyvalent ions in the system is to make use of sequestrants in the system. These sequestrants absorb polyvalent cations which are present and prevent premature gelation. Subsequently they control the viscosity and the velocity of gelation of the fabricated product.

Effect of Concentration

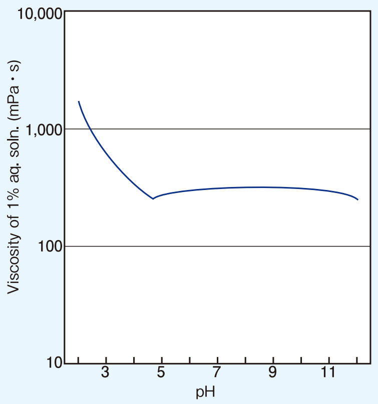
The viscosity of aqueous sodium alginate solutions increases logarithmically with increase of concentration.



●Viscosity vs level of Na-alginate conc.

Effect of pH

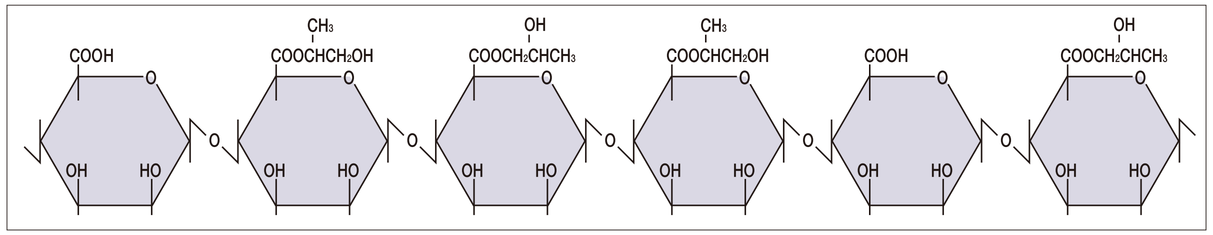
Decrease in pH of the solution causes transformation of soluble alginate anion to insoluble alginic acid, and results in higher viscosity. At pH 2.0 or below, the alginic acid precipitates.



●Viscosity vs pH

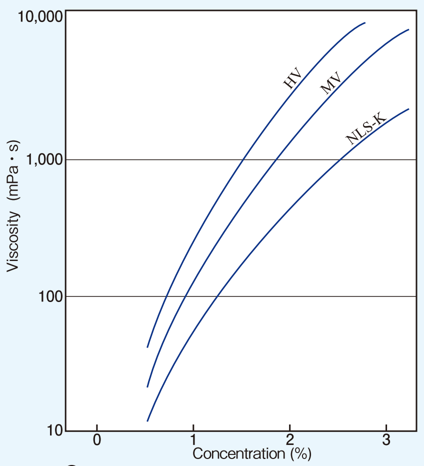
KIMILOID Propylene Glycol Alginate（PGA）

KIMILOID, KIMICA's propylene glycol alginate (PGA) is made by the esterification of the carboxyl groups in alginic acid with propylene glycol groups. Use of PGA overcomes problems which can arise when using unesterified alginates. With unesterified alginates undesired gelation or precipitation can occur, especially at acidic pH values and in the presence of a high level of divalent cations. PGA can therefore be used with ease in low pH products and in products with high levels of divalent cations.



Properties of KIMILOID aqueous solution

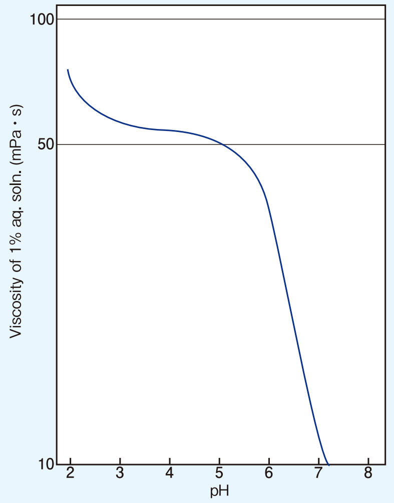
- It dissolves in both cold and hot water giving high viscosity,
- 1% aqueous solution has pH 3-4,
- High affinity with water may cause undissolved lumps. Therefore good agitation is required when dissolving PGA.



●Viscosity vs KIMILOID Conc.

Low pH stability of aqueous solutions of KIMILOID

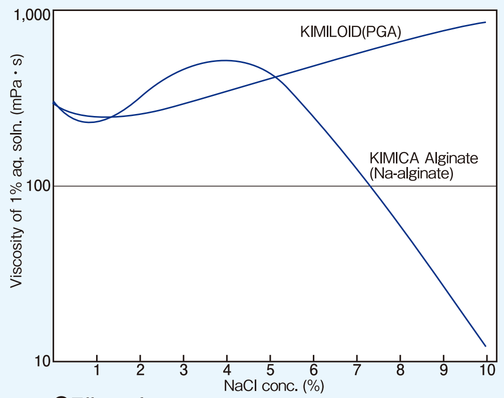
- KIMILOID exhibits very stable viscosity at pH 3-5, and is effective as a thickening agent and emulsion stabllizer for acidic foods.



●pH vs Viscosity (KIMILOID NLS-K)

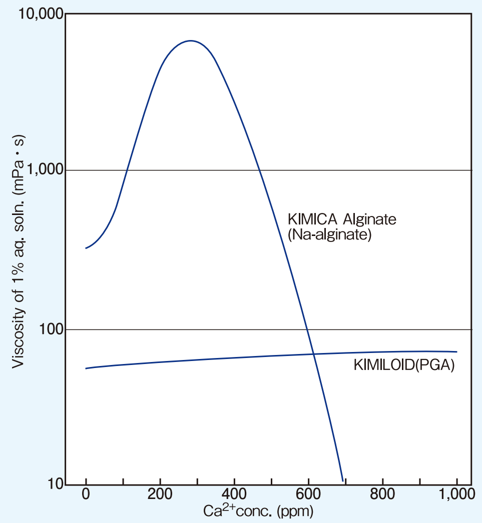
High salt tolerance of an aqueous solution of KIMILOID

- High concentration of monovalent cations, such as NaCl, cause alginate molecules to collapse and to precipitate through salting out. However, KIMILOID PGA does not behave in this way and is stable even at high levels of monovalent inorganic salts.



●Effect of monovalent electrolytes

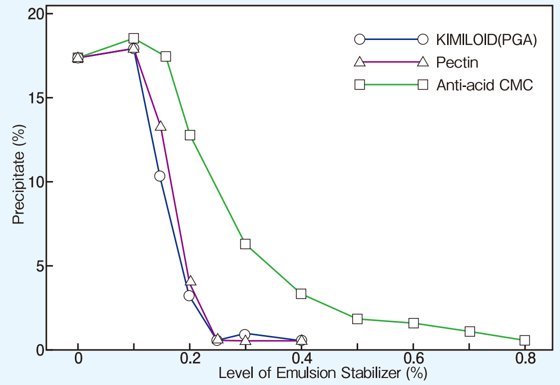
- KIMILOID does not gel even when polyvalent cations are present and therefore, has very stable performance as a thickening agent, emulsifier or emulsion stabilizer.



●Effect of polyvalent cations

KIMILOID, Emulsion Stabilizer

- KIMILOID has high foaming characteristics itself, and is an excellent foam stabilizer.
  Also, it is effective as an emulsifier in oil and water systems because of the effect of the propylene glycol groups in KIMILOID.



●Effect of Stabilizers on acidic milk protein stabilization
(Weight of precipitate from a fat-free 3% crude protein solution, after homogenizing and centrifuging at 3,000rpm for 20 minutes)

Selection Guide (Product List)

Sodium Alginate

Fine Food & Pharmaceutical grades :

KIMICA ALGIN I - series

	Viscosity (1% solution at 20℃)
IL-2	20 ～ 50 mPa·s
IL-6	50 ～ 80 mPa·s
I-1	80 ～ 200 mPa·s
I-3	300 ～ 400 mPa·s
I-5	500 ～ 600 mPa·s
I-8	800 ～ 900 mPa·s

Industrial Fine grades :

KIMICA ALIGN B - series

	Viscosity (1% solution at 20℃)
BL-2	20 ～ 50 mPa·s
BL-6	50 ～ 80 mPa·s
B-1	100 ～ 200 mPa·s
B-3	300 ～ 400 mPa·s
B-5	500 ～ 600 mPa·s
B-8	800 ～ 900 mPa·s

Low viscosity special-purpose grades :

KIMICA ALGIN ULV - series

	Viscosity (10% solution at 20℃)
ULV-L3	20 ～ 50 mPa·s
ULV-L5	30 ～ 60 mPa·s
ULV-1	100 ～ 200 mPa·s
ULV-3	300 ～ 400 mPa·s
ULV-5	500 ～ 600 mPa·s
ULV-20	1800 ～ 2300 mPa·s

High stiffness gelation special-purpose grades :

KIMICA ALGIN High G - series

	Viscosity (at 20℃)
ULV-L3G	20 ～ 50 mPa·s (10%)
IL-6G	50 ～ 80 mPa·s (1%)
I-1G	100 ～ 200 mPa·s (1%)
I-3G	300 ～ 400 mPa·s (1%)

General-purpose Industrial grades :

KIMITEX - series

	Viscosity (1% solution at 20℃)
LL	30 ～ 60 mPa·s
L	100 ～ 200 mPa·s
M	300 ～ 400 mPa·s
H	500 ～ 600 mPa·s

Propylene Glycol Alginate

KIMILOID - Emulsion Stabilizer

	Viscosity (1% solution at 20℃)
LLV	10 ～ 30 mPa·s
NLS-K	30 ～ 60 mPa·s
LV	60 ～ 100 mPa·s
MV	100 ～ 150 mPa·s
HV	150 ～ 250 mPa·s
LVC	70 ～ 170 mPa·s
HVC	200 ～ 600 mPa·s

KIMILOID - Beer Foam Stabilizer

	Viscosity (2% solution at 25℃)
BF	50 ～ 200 mPa·s

Alginic Acid

KIMICA ACID	SN	(NF)
KIMICA ACID	SF	(FCC)
KIMICA ACID	SB	(BP)
KIMICA ACID	SC	(BPC)

Other Salts

KIMICA ALGIN K	(Potassium Alginate)
KIMICA ALGIN Ca	(Calcium Alginate)
KIMICA ALGIN NH	(Ammonium Alginate)
KIMICA ALGIN Z	(Zinc Alginate)

Super clear, Transparent grades :

SKAT - series

Welding rod grades :

WELCOAT - series

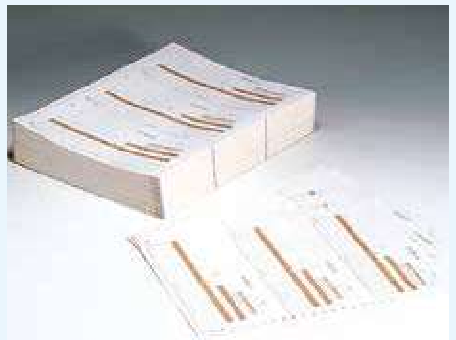
Intermediate grades and special grades other than the above are also available upon request.
Please check with your local sales representative.









Major Applications

- ●Food,
- ●Pharmaceutical,
- ●Textile printing,
- ●Cosmetics,
- ●Pet Foods,
- ●Aqua cultivation (hydroponics),
- ●Welding rods,
- ●Paper making,
- ●Construction,
- ●Ceramics,
- ●Water treatment,
- ●Fertilizer,
- ●Agricultural chemieals,
- ●Culture medium,
- ●Micro-encapsulation,

Major Functions

- ●Thickening Agent,
- ●Dispersion Stabilizer,
- ●Gelling agent,
- ●Film Former,
- ●Ion-exchanger,
- ●Coagulant,
- ●Humidifier,
- ●Emulsifier,
- ●Emulsion Stabilizer,