# CELLOGEN

Sodium Carboxymethyl Cellulose

DAI-ICHI KOGYO SEIYAKU CO., LTD.

# Contents

CELLOGEN Features —		- 1
Structural Formula and Manufacturing Pro	ocess —	_ (
Grades and Specifications —		_ 4
General Properties	* 0	- :
CELLOGEN Solution Rheology —		_ (
Viscosity —		_ ′
Physical and Chemical Properties —		_ '
Applications —		- 1
Handling & Storage Instructions / Notes		- 12

## **CELLOGEN Features**

CELLOGEN, our synthetic gum product series, is a water-soluble cellulose ether generally known as CMC (sodium carboxymethyl cellulose) or cellulose gum.

Compared with natural or other synthetic gums, CELLOGEN, as a cellulose derivative, has many unique features. It is widely used for textiles, foods, pharmaceuticals, cosmetics, paper, ceramics, building materials, civil engineering, drilling and agriculture as a binder, dispersant, thickener and film-forming agent.

Our company is one of the world's largest CMC manufacturers and our innovative technology has won it worldwide acclaim.

#### **Features**

- (1) Easily soluble in cold or hot water to make viscous solutions.
- (2) Very little viscosity change over time.
- (3) Excellent emulsion dispersion and solid dispersion.
- (4) Forms a strong, transparent film with an adhesive effect.
- (5) Less susceptible to decomposition than natural gums.
- (6) Immiscible in oil, grease and organic solvent.
- (7) Physiologically inert.
- (8) Constant and uniform quality with high purity.
- (9) Wide range of D.S. and viscosity.



Our Ohgata Plant, where all grades of **CELLOGEN** are manufactured, is ISO9002 certified since 4th September, 1998.

## Structural Formula and Manufacturing Process

CELLOGEN has a chemical structure indicated in Figure 1.

CMC with one carboxymethyl group per anhydroglucose unit is defined as 1.0 of D.S. (degree of substitution). Because each anhydroglucose unit has three OH groups, D.S. of CMC can theoretically be up to 3.0. However, in most of the commercial products, the D.S. is around 0.5 to 1.2. We can supply CMC's with the degrees of substitution as high as 1.5, as well as the regular ones. **Figure 1** illustrates a CELLOGEN structure with a D.S. of 1.0.

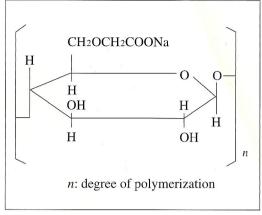
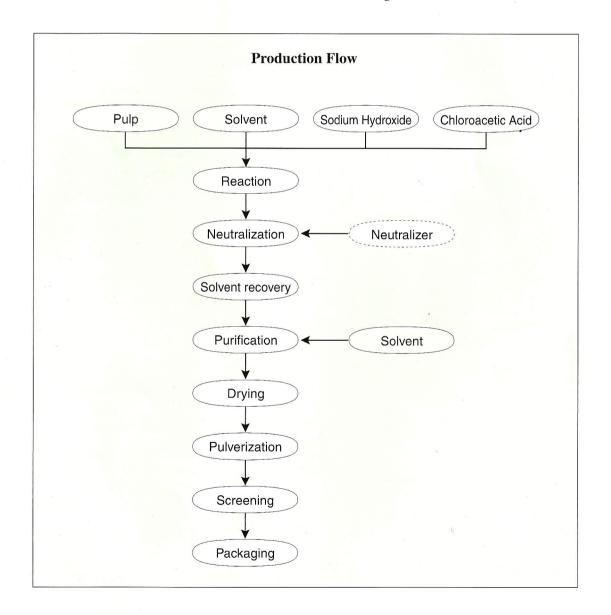


Figure 1. Structure of CMC



# Grades and Specifications

	Viscosity (mPa⋅s, at 25°C)		Purity, on a dry	Degree of
	1% Conc.	2% Conc.	basis (min.)(%)	Substitution
Purified grade				
5A		5max.	97	0.70 - 0.80
6A		5 - 11	97	0.70 - 0.80
7A		10 - 20	97	0.70 - 0.80
PR		70 - 130	98	0.60 - 0.70
WS-A		600 - 900	99	0.70 - 0.80
WS-C	150 - 250		99	0.60 - 0.70
WS-D	250 - 350		99	0.60 - 0.70
BS	350 - 500		99	0.60 - 0.70
	500 - 800	21	99	0.70 - 0.80
BS-H	500 - 1,000		99	0.55 - 0.65
HH			99	0.55 - 0.65
3H	1,000	9	99	0.55 - 0.65
4H	1,400 - 1,800	=	99	0.65 - 0.75
BSH-5	2,500 - 3,000	6 30 80		0.65 - 0.75
BSH-6	3,000 - 4,000		99	
BSH-12	6,000 - 8,000		99	0.65 - 0.75
Food grade				
F-7A	11	10 - 20	99	0.70 - 0.80
F-810A		50 - 150	99	0.75 - 0.85
F-SB	*	150 - 250	99	0.85 - 0.95
F-930A		200 - 300	99	0.85 - 0.95
F-SA		600 - 900	99	0.70 - 0.80
F-AG	8	900 - 1,500	99	0.85 - 0.95
F	150 - 250		99	0.60 - 0.70
F-SH	350 - 500		99	0.60 - 0.70
F-BSH	500 - 800		99	0.70 - 0.80
F-815C	1,000 - 2,000		99	0.80 - 0.90
	1,000 - 1,400		99	0.55 - 0.65
F-3H	1,400 - 1,800		99	0.55 - 0.65
F-4H			99	0.65 - 0.75
F-BSH-5			99	1.15 - 1.45
HE-1500F	2,500 - 3,500		99	0.65 - 0.75
F-BSH-6	3,000 - 4,000			
F-6HS9	3,000 - 4,000		99	0.80 - 0.90
F-BSH-12	6,000 - 8,000		99	0.65 - 0.75
F-EPH	9,000 - 13,000		99	0.80 - 0.90
FDA grade				. =
HP-8A		30 - 50	99.5	0.70 - 0.80
HP-810A		50 - 150	99.5	0.75 - 0.85
HP-SB		150 - 250	99.5	0.85 - 0.95
HP-930A		200 - 300	99.5	0.85 - 0.95
HP-SA		600 - 900	99.5	0.70 - 0.80
HP-F	150 - 250		99.5	0.60 - 0.70
HP-SH	350 - 500		99.5	0.60 - 0.70
HP-3H	1,000 - 1,400		99.5	0.55 - 0.65
HP-3HS	1,500 - 2,000		99.5	0.65 - 0.75
HP-5HS	2,500 - 3,500		99.5	0.65 - 0.75
HP-6HS	3,000 - 4,000		99.5	0.65 - 0.75
HP-6HS9	3,000 - 4,000		99.5	0.80 - 0.90
HP-12HS	9,000 - 13,000		99.5	0.65 - 0.75

Notes: Moisture: 10% max. for all grades

Appearance: powdery and granular (SG) types are available.

Values given are for packaged products.

Packaging: CELLOGEN is packaged in a three-ply paper bag with an inner heat sealed polyethylene liner.

Net weight is either 50 pounds (22.7kg) or 20 kg per bag.

### **General Properties**

CELLOGEN properties depend on the average D.S. and the average degree of polymerization. Various combinations of D.S. and degrees of polymerization allow the series of CELLOGEN to meet a variety of needs in practical applications.

#### (1) Moisture absorption

CELLOGEN, like many other water-soluble gums, is hydroscopic. The equilibrium moisture content in CELLOGEN increases as humidity increases, and decreases as the temperature rises (Figure 2).

The higher the D.S. is, the more moisture in the air CMC is likely to absorb. If the CELLOGEN package is opened and left in a highly humid environment for a long period of time, its moisture content can exceed 20%. The powdery state of CELLOGEN does not change while the moisture content is up to 15%. Beyond 20%, some particles stick to each other and the fluidity of the powder is deteriorated. The weight of CELLOGEN increases considerably with moisture absorption. Therefore, any open bag of CELLOGEN must be placed in an airtight container or the bag closed and stored in a dry place.

#### (2) Dissolving CELLOGEN

CELLOGEN, like other water-soluble polymers, shows a swelling phenomenon before dissolution. When a large amount of CELLOGEN solution is to be prepared, quicker dissolution is achieved when each particle is uniformly swollen. When CELLOGEN is hastily put into water, viscous lumps —"fish eyes"— can form. The following methods are recommended for quick dissolution of CELLOGEN.

- 1) Add CELLOGEN slowly to water with moderate stirring. Use of a polymer eductor is recommended.
- CELLOGEN can be pre-wet with water-miscible solvents such as alcohol or glycerin in advance, and then slowly put into water with moderate stirring.
- 3) If any other powdered additives are to be added to the solution, premix them well with CELLOGEN in advance and then put into water.

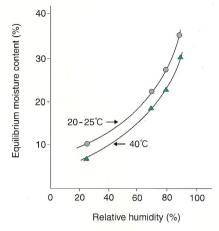


Figure 2. Effect of relative humidity on equilibrium moisture content

## **CELLOGEN Solution Rheology**

Some liquids such as water, glycerin, silicone oil etc., are Newtonian fluids; when their viscosities are measured with a rotational viscometer, the results of each will be the same whether they are measured at a high or low rotation speed. On the other hand, CELLOGEN solutions, which are non-Newtonian fluids, show lower viscosities at higher rotation speeds. That is, since the viscosity of CELLOGEN varies according to the measuring conditions, its absolute viscosity cannot be determined. Therefore, "apparent viscosity", i.e. consistency, is used to describe the property.

On a fluid curve which schematically shows the non-Newtonian fluid characteristics, the correlation between the shear rate (rotor's rpm of a viscometer) and the shear stress (torque on the viscometer) does not yield a straight line but a curve (**Figure 3a**).

CELLOGEN solutions are also known as pseudoplastic fluids. When the shear rate is low, the consistency appears high, i.e., the shear stress becomes high, and on the fluid curve, it seems as if it is a plastic fluid with a yield point. (By definition, at a yield point, a solution starts to flow.)

#### (1) CELLOGEN solution thixotropy

Thixotropy is a character of a substance that shows different states when it is static versus when being agitated. A CELLOGEN solution, when it is static, is likely to form a network structure due to molecular entanglement and/or interaction with water molecules; this state is called "gel". When the solution is agitated, the network structure is broken and the gel disappears. Thus, the consistency appears higher under static conditions and lower when being agitated.

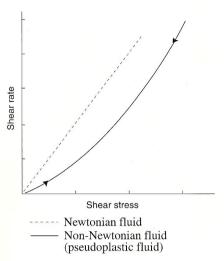


Figure 3a. Fluid curves

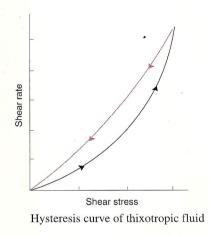


Figure 3b. Fluid curve

**Figure 3b** shows the thixotropic solution's behavior as a fluid curve. When the shear rate increases and decreases continuously, the correlation between the shear rate and the shear stress in both cases do not correspond but appear as two different curves, i.e., a hysteresis curve. Thixotropy of CELLOGEN solutions is not very apparent at lower concentrations, however, it becomes prominent at higher concentrations. Thixotropy decreases as D.S. increases.

#### (2) CELLOGEN solution viscoelasticity

CELLOGEN solutions are typical viscoelastic fluid; they are highly viscous and elastic. For example, when a mixing bar is rotated in the solution, the fluid creeps up along the bar. This phenomenon is called the Weissenberg effect, and is not observed in a sodium silicate solution (water glass) that has a similar viscosity.

#### (1) Viscosity and average degree of polymerization

The viscosity of CELLOGEN depends mainly on the average degree of polymerization of the cellulose chains forming the structure framework. As shown in **Figure 4**, a nearly linear relationship exists between viscosity and the average degree of polymerization. The average degrees of polymerization of some CELLOGEN grades are listed in **Table 1**.

	Average degree of polymerization	Average molecular weight
7A	120 - 150	27,000 - 33,000
PR	220 - 250	47,000 - 54,000
F-SB	250 - 300	57,000 - 69,000
WS-A	460 - 500	100,000 - 110,000
BS-H	800 - 900	180,000 - 190,000
3Н	1,000 - 1,200	210,000 - 250,000
F-815C	1,000 - 1,250	230,000 - 290,000
HE-1500F	1,300 - 1,400	335,000 - 361,000
BSH-12	1,600 - 1,800	330,000 - 380,000

Table 1. Degrees of polymerization and molecular weights of CELLOGEN grades

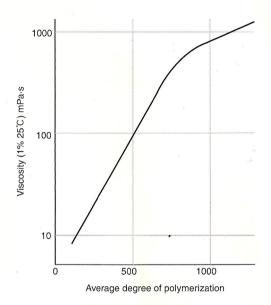


Figure 4. Relationship between viscosity and average degree of polymerization of CELLOGEN 1% aqueous solution

#### (2) Viscosity and concentration

The relationships between concentration and various grades of CELLOGEN are shown in **Figure 5a.** The viscosity is roughly logarithmicly proportional to concentration. CELLOGEN yields considerably high viscosity even at low concentrations; this property of CELLOGEN enables itself to work as a superior thickener.

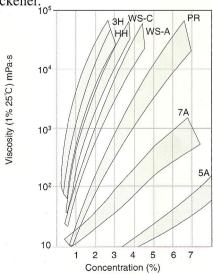


Figure 5a. Relationship between concentration and viscosity of various grades of CELLOGEN

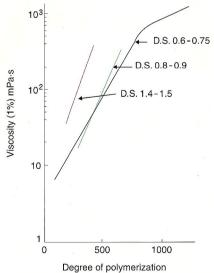


Figure 5b. Relationship between viscosity and degree of polymerization

#### (3) Viscosity and temperature

The viscosity of CELLOGEN aqueous solutions is higher at lower temperatures and decreases as temperature rises. This change is reversible within the range of temperature up to 50 to 60°C; the viscosity does not permanently change within this range. Regarding lower temperatures, permanent viscosity change never occurs even if it has been frozen. As shown in **Figure 6**, the relationships between viscosity and temperature of various CELLOGEN solutions result in similar curves, regardless of the grades or concentrations of the CELLOGEN used.

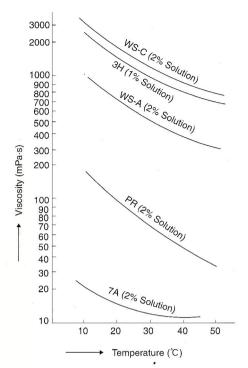


Figure 6. Viscosity change of CELLOGEN solutions against temperature

# Physical and Chemical Properties

#### (1) Effect of temperature

Viscosity changes are reversible unless CELLOGEN solutions are heated over 60°C. Temperatures over 80°C may result in an irreversible viscosity drop.

#### (2) Effect of agitation

Even at low concentrations, a CELLOGEN solution forms a weak network structure by its molecular entanglement and interaction with water molecules. When the solution is radically agitated, the structure is broken and viscosity is temporarily reduced. However, once the solution returns to a static state, the structure is re-formed and the viscosity increases again by its thixotropic nature. Even though a stronger agitation results in a slight viscosity drop compared to the initial state, the structure recovers in time. This is particularly remarkable at higher concentrations and lower D.S. When preparing a CELLOGEN solution, mild agitation is preferable which is closer to natural dissolution. **Figure 7** shows the results of the experiment of time-related viscosity changes according to agitation strength.

#### (3) Effect of pH

At the pH of 7 to 9, the viscosity of CELLOGEN solutions is at its maximum and is very stable. The viscosity remains constant within the pH range 5 to 10 (**Figure 8**).

CELLOGEN is more easily soluble in an alkaline solution than in a neutral one. A pH of 10.0 or greater can cause depolymerization of CELLOGEN and will result in decrease in viscosity. When acid is added to a CELLOGEN solution, the solubility decreases as Na salt is partially substituted with H. In a strong acid solution (pH 3.0 - 4.0), semi-soluble gel is partially developed and consequently, the viscosity increases. Below the pH 3, the CELLOGEN becomes completely immiscible and forms CMC acid precipitates.

CELLOGEN's acid- and alkali-resistance increases as D.S. increases. Low-viscosity products are more resistant to acid/alkali than high-viscosity ones.

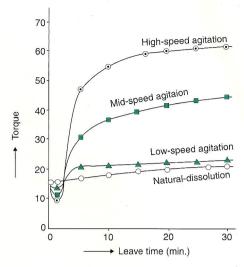


Figure 7. Difference of time-course viscosity change according to agitating strength (shown by torque)

CELLOGEN WS-C 2.7% solution

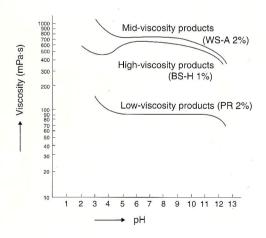


Figure 8. Effect of pH on viscosity

#### (4) Effects of salts

Salts in a CELLOGEN solution suppresses molecular dissociation by the counter-ion effect. At the same time, the salts' affinity for water diminishes the CMC's affinity for water. Consequently, the dissolving form of molecules changes, resulting in the changes in viscosity and state.

When a monovalent metallic salt is put in a CELLOGEN solution, CMC maintains its solubility, while its viscosity decreases according to the salt's affinity for water. For instance, Glauber's salt (sodium sulfate decahydrate) reduces the solution's viscosity more sharply than sodium chloride.

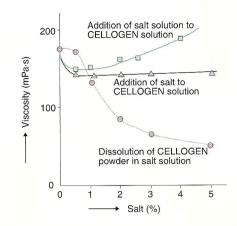


Figure 9. Viscosity change of CELLOGEN WS-C 1% solutions by salt addition method

When a divalent metallic salt is put in a CELLOGEN solution, Na ions are replaced by metallic ions and consequently, the solution either gels or completely precipitates as CMC metallic salt, depending on the amount of metallic ions. In general, trivalent ions are more likely to form insoluble precipitates than divalent ions.

The effects of salts on CELLOGEN solutions vary according to the mixing method. The biggest effect is observed when CELLOGEN powder is added to a salt solution, and the second biggest when solid salts are added to a CELLOGEN solution. The effect is the smallest when CELLOGEN and salts are mixed together both as solutions. Figure 9 shows the results of the experiment.

#### (5)Biological stability

Compared with natural gums, CELLOGEN solutions are less likely to be deteriorated by microorganisms. However, when used with water containing a large number of microorganisms in a hot environment, decomposition of the solution may occur. As a result, the viscosity drops and the solution cannot perform as originally designed.

The effect of microorganisms on CELLOGEN is that the enzyme called cellulase, which is produced by the microorganisms, will decompose the cellulose chains. Thus, finest care should be taken to keep the solution away from microorganisms (molds and/or bacteria). The water can be sterilized by heating at high temperatures (at 80°C for 30 min. or 100°C for several min.), and the solution should be stored in a clean airtight container. Bactericides are also effective. CELLOGEN's with higher D.S. are more resistant to microorganisms.

# Applications

#### **Applications**

Fields	Functions	Use
Textiles	Thickening	Printing, warp sizing, finishing, thermosol dyeing
Foods	Water retention, texture improvement, thickening, suspension aid, additive for low calorie food	Ice creams, sorbets, frozen desserts, hams, sausages, canned fish, juices, powdered juices, syrups, powdered soups, instant Chinese noodles, cake/sponge mixtures, biscuits, crackers, pet foods, fish feeds
Cosmetics & Pharmaceuticals	Suspension aid, water retention, thickening, binding, plasticizing, foam stabilizing	Barium meal, ointment bases, tablets, toothpastes, shampoos, hand creams, lotions
Paints	Stabilizing, thickening, paintability improvement	Emulsion paints, water paints
Ceramics	Binding, plasticizing, peptizing, dispersing, penetration/adhesion improvement	Clay mud, glazes, painting/sanding
Drilling	Thickening, F.L. reduction	Rotary drilling in mud, turbine drilling in a petroleum-/gas-well
Agriculture	Dispersing, binding, fixing	Wettable pesticide powder, pesticide granulating agent, insecticide
Adhesives	Adhesiveness	Wall paper paste, leather paste, sealing for envelopes
Paper	Surface sizing, water retention, microcapsulation, pitch dispersing	Beater treating, calendar coating, off-set printing, non-carbon paper
Others	Casting, dispersing, binding, foam stabilizing, air-entrainment, flocculation	Rubber manufacturing (mold release, dispersion of titanium oxide and zinc white), oval briquettes, fire-proof bricks

