CELLULOSE ETHERS

1. General Considerations

Alkylation of cellulose yields a class of polymers generally termed cellulose ethers. Most of the commercially important ethers are water-soluble and are key adjuvants in many water-based formulations. The most important property these polymers provide to formulations is rheology control, ie, thickening and modulation of flow behavior. Other useful properties include water-binding (absorbency, retention), colloid and suspension stabilization, film formation, lubrication, and gelation. As a result of these properties, cellulose ethers have permeated a broad range of industries including foods, coatings, oil recovery, cosmetics, personal care products, pharmaceuticals, adhesives, printing, ceramics, textiles, building materials, paper, and agriculture.

Estimates from SRI International figures indicate that the world consumption, excluding eastern European countries and the former Soviet Union, of all grades of cellulose ethers in 1987 was about 230,000 t (1). Cellulose ethers represent a mature industry with annual sales of over one billion dollars and annual growth rate averaging 2–3% per year. The U.S. consumption in 1987 was approximately 69,000 t, Western Europe about 116,000 t, and Japan about 22,000 t. Prices for the principal products range from about $1.65/kg for crude grades of sodium carboxymethylcellulose to over $11/kg for purified hydroxypropylcellulose. The highest volume cellulose ethers, the industry workhorses, are sodium carboxymethylcellulose, hydroxyethylcellulose, and hydroxypropylmethylcellulose. Cellulose ethers as a class compete with a host of other materials including natural gums, starches, proteins (qv), synthetic polymers, and even inorganic clays (see CARBOHYDRATES; GUMS). They provide effective performance at reasonable cost and are derived from a renewable, natural resource.

Cellulose ethers are manufactured by reaction of purified cellulose with alkylating reagents under heterogeneous conditions, usually in the presence of a base, typically sodium hydroxide, and an inert diluent. Cottonseed linter fiber and wood fiber are the principal sources for cellulose. Purified cellulose cotton linters, commonly termed chemical cottons, are generally of higher purity and higher maximum molecular weight than purified cellulose from dissolving grades of wood pulp. The base, in combination with water, activates the cellulose matrix by disrupting hydrogen-bonded crystalline domains, thereby increasing accessibility to the alkylating reagent. This activated matrix is commonly termed alkali cellulose (2–6). The base also promotes the etherification reaction. The several purposes of the inert diluent are to suspend/disperse the cellulose, provide heat transfer, moderate reaction kinetics, and facilitate recovery of the product. Crude grades of cellulose ethers, most notably sodium carboxymethylcellulose, may be made in the absence of any diluent. Reactions are typically conducted at elevated temperature, $\sim$50 to 140°C, and under nitrogen to inhibit oxidative molecular weight degradation of the polymer (7,8), if so desired. After reaction, crude grades are simply dried, ground, and packed out; purified grades require removal of byproducts in a separate operation prior to drying. Various additives, such as colloidal silicas, may be added in small amounts to some

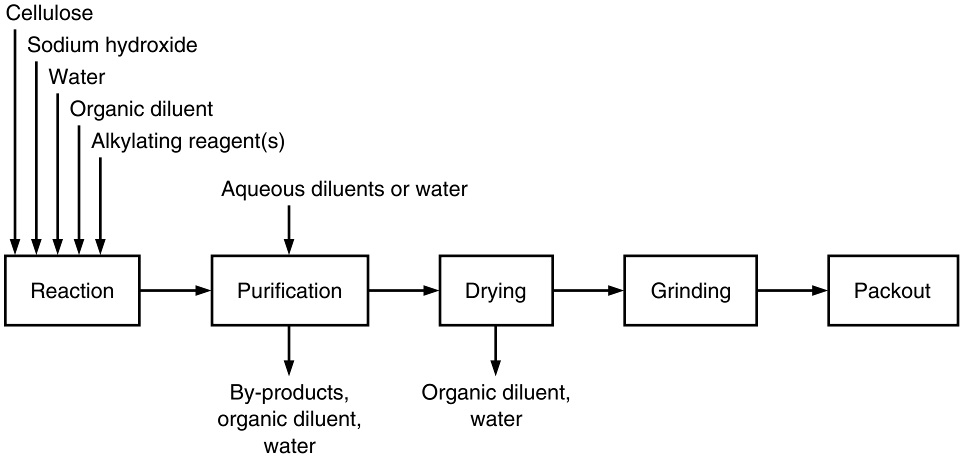
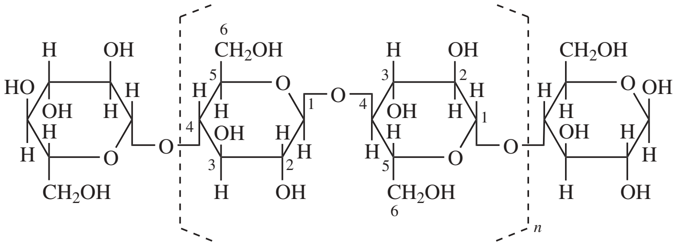


Fig. 1. Unit operations for the manufacture of purified cellulose ethers.

products prior to drying or before packout to improve dry handling properties. In addition to these unit operations, schematically outlined in Figure 1, a molecular weight reduction operation may be included in the process at any of several points, most notably either in the reaction vessel (before, during, or after the alkylation reaction), after purification before drying, or treatment of dry material (9–11). Hydrogen peroxide is commonly used, though deliberate degradation may also be induced through controlled alkaline-catalyzed autoxidation with oxygen (air) in the reactor. Acids can also be used to cleave the cellulose chain (12,13).

An important characterization parameter for cellulose ethers, in addition to the chemical nature of the substituent, is the extent of substitution. As the Haworth representation of the cellulose polymer shows, it is a linear, unbranched polysaccharide composed of glucopyranose (anhydroglucose) monosaccharide units linked through their 1,4 positions by the β anomeric configuration.



The structurally similar starch amylose polymer is linked through the α anomeric configuration. The three hydroxyl functions per anhydroglucose unit are noteworthy; these hydroxyls are the active sites for ether formation.

The extent of substitution is described as the degree of substitution (DS), defined as the average number of hydroxyl groups substituted per anhydroglucose unit. Excluding the terminal residues, each anhydroglucose moiety has three available hydroxyl groups for a maximum DS value of three. In certain cases the alkylating reagent, such as an alkylene oxide, generates a new hydroxyl group upon reacting which can then further react to give oligomeric chains. The product is then characterized by its molar substitution (MS), the moles of reagent combined per mole of anhydroglucose unit. The ratio of MS to DS is a measure of the average chain length of the oligomeric side chains. Organosoluble ethylcellulose has a DS of 2.3–2.8. Most water-soluble derivatives have DS values of 0.4–2.0. Hydroxyalkyl ethers have MS values typically between 1.5 and 4.0.

MS and DS values are average values, placing no significance on the formal distribution of the substituents within or among polymer chains. Substituent distribution, however, is an important molecular parameter affecting solution rheology and ultimately end use properties. A classic example is offered by sodium carboxymethylcellulose (14). Depending on reaction conditions, sodium carboxymethylcellulose (CMC) of DS $\sim$0.80 can be made to exhibit a varying degree of solution thixotropy, the effect being dependent not so much on degree of substitution but rather on the distribution of substituents.

Thixotropic solutions are characterized by a decrease in viscosity on shearing followed by a time-dependent increase after the shear stress is removed. A plot of shear rate versus shear stress reveals a hysteresis loop. Association among polymer chains via electrostatic, hydrogen-bonding, or hydrophobic effects can lead to thixotropy. Carboxymethyl substituent uniformity along the polymer chain affects thixotropic behavior of CMC because regions of contiguous unsubstituted anhydroglucose units, ie, blocks, among polymer chains tend to associate through hydrogen bonding (15). The extent of blockiness is controlled by reaction conditions. Solution thixotropy is important in applications requiring suspension or stabilization of particulates.

As substituent uniformity is increased, either by choosing appropriate reaction conditions or by reaction to high degrees of substitution, thixotropic behavior decreases. CMCs of DS $\geq$ 1.0 generally exhibit pseudoplastic rather than thixotropic rheology. Pseudoplastic solutions also decrease in viscosity under shear but recover instantaneously after the shear stress is removed. A plot of shear rate versus shear stress does not show a hysteresis loop.

Other examples illustrating the effect of substituent distribution on properties include: (*1*) enzymatic stability of hydroxyethylcellulose (16,17); (*2*) salt compatibility of carboxymethylcellulose (18,19); and (*3*) thermal gelation properties of methylcellulose (20). The enzymatic stability of hydroxyethylcellulose is an example where the actual position of the substituents within the anhydroglucose units is considered important. Increasing substitution at the C2 position promotes better resistance toward enzymatic cleavage of the polymer chain. Positional distribution is also a factor in the other two examples.

^{13}C-nmr is the premier method for the compositional and structural characterization of cellulose ethers (21–27). Another analytical method is based on chromatography of hydrolyzates (28). The results show that the reactivity of the three hydroxyl groups can vary significantly depending on the alkylating reagent, the type of reaction, and reaction conditions. For most cellulose ethers, substitution occurs primarily at the C2 and C6 hydroxyl groups (29).

Aside from the chemical nature of the substituent and its DS (MS) and distribution, solution viscosity, ie, polymer molecular weight, is another important characterization parameter. Generally, manufacturers supply cellulose ethers in different viscosity grades, made by choosing a cellulose furnish of appropriate molecular weight or by reducing the molecular weight during processing (9–11). Most manufacturers specify solution viscosity data and not polymer molecular weight in their technical literature; however, molecular weight can be estimated from the classical Mark-Houwink equation:

$$[\eta] = KM^a$$

where $[\eta]$ is intrinsic viscosity, K and a are empirically derived constants, and M is the viscosity-average molecular weight, which approximates the weight-average molecular weight. Values of K and a for various cellulose ethers are available (30–32).

Molecular weight from solution viscosity measurements represents an average value of polymer chain lengths. The distribution of chain lengths making up a polymer fraction is commonly termed molecular weight distribution (MWD), a parameter that can influence performance properties, particularly mechanical properties of films. Size exclusion chromatography (sec), also termed gel-permeation chromatography (gpc), has been the classical method for determining MWD. However, the lack of suitable columns hindered development of aqueous sec methods for water-soluble polymers until the 1980s. Now, because of the development of high performance packings and columns, the MWD of water-soluble cellulose ethers is a measurable parameter (33–36).

Many cellulose ethers contain mixed substituents (cellulose mixed ethers) in order to enhance or modify the properties of the monosubstituted derivative. For example, incorporation of low levels of hydroxypropyl or hydroxyethyl groups into methylcellulose increases its thermal gelation and flocculation temperatures in aqueous media. Carboxymethylation of hydroxyethylcellulose produces a product having excellent tolerance to mono- and divalent metal ions in solution but which readily cross-links with tri- or tetravalent ions to give highly viscoelastic gels. The solubility of ethylcellulose in organic aliphatic solvents is improved by incorporating hydroxyethyl moieties. A fairly new commercial cellulose ether composition is a mixed ether, hydroxyethylcellulose modified with hydrophobic long-chain hydrocarbyl groups (37–39). The hydrophobic groups promote polymer chain association in solution, drastically altering rheology and surface activity properties.

1.1. Health and Safety Factors.

No adverse toxicological or environmental factors are reported for cellulose ethers in general (14,39–50). Some are even approved as direct food additives, including purified carboxymethylcellulose, methylcellulose, hydroxypropylmethylcellulose, and hydroxypropylcellulose.

The only known hazard associated with cellulose ethers is that they may form flammable dusts when finely divided and suspended in air, a hazard associated with most organic substances. An explosion may result if suspended dust contacts an ignition source. Cloud and layer ignition temperatures generally vary between 290 and 410°C (51). Critical air-borne concentrations vary depending on particle size. This hazard can be minimized largely through good housekeeping and proper design and operation of handling equipment.

Another minor hazard is that water-soluble cellulose ether powders form a slippery surface when wet; therefore, spills should be cleaned promptly to avoid slipping accidents.

2. Commercial Cellulose Ethers

2.1. Sodium Carboxymethylcellulose.

Properties. Sodium carboxymethylcellulose [9004-32-4] (CMC), also known as cellulose gum, is an anionic, water-soluble cellulose ether, available in a wide range of substitution. The most widely used types are in the 0.7 to 1.2 DS range. Water solubility is achieved as the DS approaches 0.6; as the DS increases, solubility increases. The rate at which CMC dissolves depends primarily on its particle size. Finely ground material dissolves faster than coarser grades. The coarse material, however, does not agglomerate as readily when added to water and is therefore easier to disperse. The rate of dissolution also increases with increasing substitution and decreasing molecular weight, ie, viscosity. High molecular-weight grades of CMC have viscosities as high as 12,000 mPa · s(=cP) at 1% solids (as recorded on a Brookfield LVT Viscometer at 30 rpm). Lower molecular-weight CMCs have viscosities in water as low as 50 mPa · s(=cP) at 4% solids.

CMC is soluble in hot and cold water. Solutions may be pseudoplastic or thixotropic depending on molecular weight, DS, and manufacturing process. High molecular-weight, low DS CMCs tend to be more thixotropic. Solutions are viscosity stable at ambient temperature over a wide range of pH. In general, maximum solution viscosity and best stability are obtained at pH 7 to 9. Above pH 10, a slight viscosity decrease is observed. As pH is lowered below 4, viscosity may first increase then decrease as intermolecular associations among free acid groups start affecting solubility. CMC is not soluble in organic solvents, but dissolves in mixtures of water and water-miscible solvents such as ethanol or acetone. Low viscosity CMCs are more tolerant of higher levels of organic solvents.

Monovalent cations are compatible with CMC and have little effect on solution properties when added in moderate amounts. An exception is silver ion, which precipitates CMC. Divalent cations show borderline behavior and trivalent cations form insoluble salts or gels. The effects vary with the specific cation and counterion, pH, DS, and manner in which the CMC and salt are brought into contact. High DS (0.9–1.2) CMCs are more tolerant of monovalent salts than lower DS types, and CMC in solution tolerates higher quantities of added salt than dry CMC added to a brine solution.

CMC is compatible with most water-soluble nonionic gums over a wide range of concentrations. When a solution of CMC is blended with a solution of a nonionic polymer such as hydroxyethylcellulose or hydroxypropylcellulose, a synergistic effect on viscosity is usually observed. Such blends produce solution viscosities considerably higher than would ordinarily be expected. This effect is reduced if other electrolytes are present in the system.

Some typical properties of commercial CMCs are given in Table 1.

Manufacture. Common to all manufacturing processes for CMC is the reaction of sodium chloroacetate [3926-62-3] with alkali cellulose complex

Table 1. **Typical Properties of Purified CMC**[a]

Property	Value
Powder	
appearance	white to off-white
assay, dry basis, min %	99.5
moisture, max %	8.0
browning temp, °C	227
charring temp, °C	252
bulk density, g/cm^3	0.75
molecular weight, M_w	$9.0 \times 10^4 - 7.0 \times 10^5$
Solution	
viscosity, Brookfield, 30 rpm, $mPa \cdot s (=cP)$	
at 1% solids (high M_w)	~6000
at 4% solids (low M_w)	~50
sp gr, 2% at 25°C	1.0068
pH, 2%	7.5
surface tension, 1%, mN/m(= dyn/cm)	71
refractive index, 2% at 25°C	1.3355
Film	
refractive index	1.515

[a] Ref. 14.

represented here as R_{cell} OH:NaOH:

$$R_{cell}OH + NaOH + H_2O \longrightarrow R_{cell}OH : NaOH$$

$$R_{cell}OH : NaOH + ClCH_2COO^-Na^+ \longrightarrow R_{cell}OCH_2COO^-Na^+ + NaCl + H_2O$$

sodium carboxymethylcellulose

A by-product is sodium glycolate [2836-32-0] (sodium hydroxyacetate):

$$ClCH_2COO^-Na^+ + NaOH \longrightarrow HOCH_2COO^-Na^+ + NaCl$$

Generally, monochloroacetic acid [79-11-8] (MCA) is added to the reaction slurry containing sufficient excess sodium hydroxide to neutralize the MCA and effect its reaction. The use of esters of MCA has also been reported (52). Common reaction diluents are isopropyl alcohol, *t*-butyl alcohol, or ethyl alcohol (53,54). Dimethoxyethane has also been reported to be effective (55). The product is isolated and washed with aqueous alcohol or acetone to remove by-product salts. Unpurified crude grades are generally prepared in the absence of diluents (56–59).

Economic Aspects. CMC is the most widely used cellulose ether. Excluding the former Soviet Union and Eastern Bloc countries, from which little data are available, world consumption of crude and purified grades totaled approximately 123,000 metric tons in 1987 (Table 2). Annual growth rate is nominal at 1–2%. The total volume in the United States declined in the 1980s from ~32,000 metric tons in 1981 to ~19,500 in 1987 because of decreased oil well drilling activity, an important outlet.

Table 2. **World Supply and Demand for CMC[a], 10^3t**

Region	Capacity[b]	Production	Consumption	Imports	Exports
United States	26	19.5	27.5	10.0	4.0
Western Europe	184	99	66	1	33
Japan	44	25	16	<1	9
Canada, Latin America, other Asia			13		
Total	*254*	*143.5*	*122.5*		

[a] In 1987 (1).

[b] Crude and purified grades, expressed in 100% CMC.

In the United States Aqualon Co., a Hercules Incorporated Company, is the largest producer, followed by Carbose Corp. and MAK Chemical Corp. Western Europe has about 14 companies manufacturing CMC; the five largest are Metsa Serla in Finland, Aqualon France SA in France, Hoechst AG in Germany, Billerud AB in Sweden, and AKZO in The Netherlands and Italy. Among the six producers in Japan, Dai-ichi Kogyo Seiyaku (DKS) and Diacel Chemical Industries are the two largest.

Specifications and Standards; Test Methods. Certain types of purified sodium carboxymethylcellulose meet standards set by the *U.S. Code of Federal Regulations* (CFR) Title 21, Section 182.1745, substances that are generally recognized as safe (GRAS). The FDA defines the direct food additive as the sodium salt of carboxymethylcellulose, not less than 99.5% on a dry weight basis, with a maximum substitution of 0.95 carboxymethyl groups per anhydroglucose unit, and with a minimum viscosity of 25 $\text{mPa}\cdot\text{s}(=\text{cP})$ in a 2% (by weight) aqueous solution at 25°C.

Cellulose gum is the accepted common name for purified CMC. It may be used in milk products, dressings, jellies, syrups, beverages, and other select products. It is permitted in food contact and packaging applications.

Sodium carboxymethylcellulose is listed in the 1990 *United States Pharmacopeia* under the categories of pharmaceutic aid (suspending agent, tablet binder, viscosity-increasing agent), and cathartic tablets.

Procedures for the analysis of CMC are available in manufacturers' bulletins (14).

Uses. CMC is an extremely versatile polymer, and it has a variety of applications. A sampling of significant applications is given in Table 3. A more extensive listing can be found in reference 14.

2.2. Hydroxyethylcellulose. *Properties.* Hydroxyethylcellulose [9004-62-0] (HEC), is a nonionic polymer. Low hydroxyethyl substitutions ($\text{MS} = 0.05-0.5$) yield products that are soluble only in aqueous alkali. Higher substitutions ($\text{MS} \geq 1.5$) produce water-soluble HEC. The bulk of commercial HEC falls into the latter category. Water-soluble HEC is widely used because of its broad compatibility with cations and the lack of a solution gel or precipitation point in water up to the boiling point. The MS of commercial HEC varies from about 1.8 to 3.5. The products are soluble in hot and cold water but insoluble in hydrocarbon solvents.

Table 3. **Applications for CMC**[a]

Industry	Application	Function
foods	frozen desserts	inhibit ice crystal growth
	dessert toppings	thickener
	beverages, syrups	thickener, mouthfeel
	baked goods	water-binder, batter viscosifier
	pet food	water-binder, thickener, extrusion aid
pharmaceuticals	tablets	binder, granulation aid
	bulk laxatives	water-binder
	ointments, lotions	stabilizer, thickener, film-former
cosmetics	toothpaste	thickener, suspension aid
	denture adhesives	adhesion promoter
	gelled products	gellant, film-former
paper products	internal additive	binder, improve dry-strength
	coatings, sizes	water-binder, thickener
adhesives	wallpaper paste	adhesion promoter, water-binder
	corrugating	thickener, water-binder, suspension aid
	tobacco	binder, film-former
lithography	fountain, gumming	hydrophilic protective film
ceramics	glazes, slips	binder (promotes green strength)
	welding rods	binder, thickener, lubricant
detergents	laundry	soil antiredeposition aid
textiles	warp sizing	film-former, adhesion promoter
	printing paste, dye	thickener, water-binder

[a] Ref. 14.

HEC swells or becomes partly to mostly soluble in select polar solvents, usually those that are miscible with water.

Commercially, HEC is available in a wide range of viscosity grades, ranging from greater than 500 $\mathrm{mPa \cdot s (=cP)}$ at 1% solids to less than 100 $\mathrm{mPa \cdot s (=cP)}$ at 5% total solids. Because HEC is nonionic, it can be dissolved in many salt solutions that do not dissolve other water-soluble polymers. It is soluble in most 10% salt solutions and in many 50% (or saturated) salt solutions such as sodium chloride and aluminum nitrate. As a rule, the lower substitution grades are more salt-tolerant.

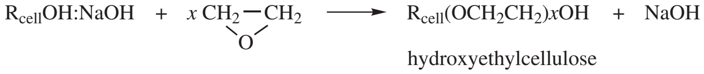
HEC is soluble in both hot and cold water; however, as with most water-soluble thickeners, the particles have a tendency to agglomerate, or lump, when first wetted with water. This is especially evident when the HEC is added to water with poor agitation. Manufacturers have eliminated the problem of lumping and slow dissolving by surface treating the particles, most commonly with glyoxal [107-22-2] (59–62). When added to water, the particles completely disperse. After an initial induction period, commonly termed the delayed hydration time, the dispersed particles begin to dissolve producing smooth, lump-free solutions. The delayed hydration time can be increased or decreased by lowering or raising, respectively, the pH. Most manufacturers supply dispersible grades.

Solutions of HEC are pseudoplastic. Newtonian rheology is approached by very dilute solutions as well as by lower molecular-weight products. Viscosities change little between pH 2 and 12, but are affected by acid hydrolysis or alkaline oxidation under pH and temperature extremes. Viscosities of HEC solutions change reversibly with temperature, increasing when cooled and decreasing when warmed.

HEC is generally compatible with other cellulosic water-soluble polymers to give clear, homogeneous solutions. When mixed with an anionic polymer such as CMC, however, interactions between the two polymers may result in synergistic behavior, ie, viscosities higher than predicted and calculated. HEC has excellent compatibility with natural gums.

Some typical properties of HEC are given in Table 4.

Manufacture. Purified hydroxyethylcellulose is manufactured in diluent-mediated processes similar to those used to produce carboxymethylcellulose except ethylene oxide [75-21-8] is used in place of MCA (63,64):



$$R_{cell}OH{:}NaOH + x\,\underset{O}{CH_2-CH_2} \longrightarrow \underset{\text{hydroxyethylcellulose}}{R_{cell}(OCH_2CH_2)xOH} + NaOH$$

A competing reaction that consumes ethylene oxide is hydrolysis to ethylene glycol and oligomeric glycol by-products.

$$NaOH + x\,\underset{O}{CH_2-CH_2} \longrightarrow HO(CH_2CH_2O)x^-Na^+$$

$$HO(CH_2CH_2O)_x^-Na^+ + H_2O \longrightarrow HO(CH_2CH_2O)_xH + NaOH$$

Because of the low boiling point of ethylene oxide, reactions are generally conducted in stirred autoclaves at elevated pressures.

Table 4. **Typical Properties of HEC**[a]

Property	Value
Powder	
appearance	white to light tan
moisture, max %	5.0
ash content (as Na_2SO_4), %	5.5
bulk density, g/cm^3	0.6–0.75
browning temp, °C	205–210
molecular weight, M_w	$9 \times 10^4 - 1.3 \times 10^6$
Solution	
viscosity, Brookfield, 30 rpm, mPa · s(=cP)	
at 1% solids (high M_w)	5000
at 5% solids (low M_w)	75
sp gr, 2%, g/cm^3	1.0033
pH	7
surface tension, mN/m(= dyn/cm)	
MS 2.5 at 0.1%	66.8
at 0.001%	67.3
refractive index, 2%	1.336
File	
refractive index	1.51
moisture content, %, at 25°C	
50% rh	6
84% rh	29

[a] Ref. 40.

Table 5. **World Supply and Demand For HEC**[a]**, 10^3 t**

Region	Capacity	Production	Consumption	Imports	Exports
United States[b]	32	20.5	20.5	1.0	3.5
Western Europe	23	17	13		
Japan	1	1	1		
Canada, Latin America, other Asia			4		
Total	*56*	*38.5*	*38.5*		

[a] In 1987 (1).

[b] Includes carboxymethylhydroxyethylcellulose, which accounts for <5%.

Economic Aspects. A breakdown of salient 1987 world supply and demand figures for HEC is given in Table 5.

Aqualon Co. and Union Carbide Corp. have manufacturing facilities in the United States and Western Europe. Hoechst AG in Europe and Fuji Chemical Co., Ltd. in Japan are the only other procedures of HEC.

Specifications and Standards; Test Methods. Hydroxyethylcellulose is included in the list of materials that are in compliance with requirements of the U.S. FDA for use in adhesives and in resinous and polymeric coatings employed on the food-contact surfaces of metal, paper, or paperboard articles, and other substrates intended for use in food packaging as specified in CFR 21. HEC made dispersible by cross-linking with glyoxal is cleared only as an adhesive and as a component of paper and paperboard in contact with food. It has not been cleared as a direct food additive.

Procedures for determining ash, moisture, solution preparation, and viscosity measurements can be found in manufacturers' product bulletins (40,41) and in ASTM D2364-69 (65).

Uses. HEC is used as a thickener, protective colloid, binder, stabilizer, and suspending agent in a variety of industrial applications. A guide to the principal uses is given in Table 6.

Table 6. **Applications for HEC**[a]

Industry	Application	Function
coatings	latex paints	thickener
	polymer emulsions	protective colloid
construction	cements, mortars	thickener, water-binder, retarder
paper	coatings, sizes	thickener, water-binder
pharmaceuticals	lotions, ointments	thickener, stabilizer, water-binder
cosmetics	toothpastes	thickener
	shampoos	thickener
	creams, lotions	thickener, stabilizer
ceramics	welding rods	water-binder, extrusion aid
	glazes	water-binder (promotes green strength)

[a] Ref. 40.

Mixed Ether Derivatives of HEC. Several chemical modifications of HEC are commercially available. The secondary substituent is generally of low DS (or MS), and its function is to impart a desirable property lacking in HEC.

Carboxymethylhydroxyethylcellulose (CMHEC). This is an anionic modification of HEC manufactured by Aqualon Co. Sodium carboxymethylhydroxyethyl-cellulose [9088-04-4] is manufactured by reaction of alkali cellulose either simultaneously or sequentially with ethylene oxide and sodium chloroacetate. Various grades, with carboxymethyl DS, CM(DS), of 0.3 to 0.5 and hydroxyethyl MS, HE(MS), of 0.7 to 2.0 are available. CMHEC has properties of both HEC and CMC. It is more compatible than CMC with salts because of the presence of nonionic hydroxyethyl groups. In saturated NaCl, only CMC with a CM(DS) ≥ 1.0 is completely soluble. CMHEC, on the other hand, is soluble with a CM(DS) as low as 0.3. CMHEC is also very tolerant of Ca^{2+} and consequently readily dissolves in seawater. Unlike HEC, CMHEC in solution may be cross-linked with trivalent cations such as Fe^{3+} and Al^{3+} to give greatly increased viscosity or three-dimensional viscoelastic gels (66).

CMHEC products are used predominantly in oil recovery applications. The high water binding capability, salt compatibility, and adsorption to clay and mineral surfaces give CMHEC ethers excellent control over high salinity fluids (67,68). Water loss in cement slurries is also reduced (69). CMHEC is also used in hydraulic fracturing fluids. Gels formed by cross-linking with multivalent cations can suspend and transport proppants into a well bore and then fracture (66,70). Some typical properties of CMHEC having a CM(DS) $\sim$0.3 and HE(MS) $\sim$0.7 are listed in Table 7.

Cationic Hydroxyethylcelluloses. These materials are manufactured by Union Carbide Corp. and National Starch and Chemical Corp., marketed under the trade names Polymer JR and Celquat, respectively (47,48). The

Table 7. **Typical Properties of Mixed Ether Derivatives of HEC**[a]

Property	CMHEC	Cationic HEC	EHEC	HMHEC
Powder				
appearance	off-white	light yellow	off-white	off-white
bulk density, g/cm^3	0.6	0.48	0.4–0.8	0.55–0.75
ash content (as Na_2SO_4), %		3	3 (as NaCl)	10 max
volatiles, %	6–8	7	8 max	5 max
Solution				
pH	6.5–10	7	6–7	6–8.5
flocculation temp in water, °C			$\sim$65	
surface tension, mN/m(= dyn/cm)			55	$\sim$62
Film				
tensile strength, MPa[b]	69[c]	14–22[c]	45–55[d]	
flexibility[e]		60–70[c]	25–35[d]	
refractive index	1.530		1.49	

[a] Refs. 39, 47, 49, 71.

[b] To convert MPa to psi, multiply by 145.

[c] At 50% rh.

[d] At 65% rh.

[e] MIT double folds.

cationic substituent on Polymer JR is presumably 2-hydroxypropyltrimethylammonium chloride (72). Celquat is presumably the reaction product of HEC with *N,N*-diallyl-*N,N*-dimethylammonium chloride (73). Their primary application is in shampoos and hair conditioners wherein the cationic moiety imparts substantivity to hair. Some typical properties of Celquat resins are given in Table 7.

Hydrophobic Hydroxyethylcelluloses. These materials are produced by stepwise or simultaneous reaction of ethylene oxide and a hydrophobic alkylating reagent. Commercial products include: ethylhydroxyethylcellulose [9004-58-9] (EHEC), manufactured by Berol Kemi AB under the Bermocoll trade name (49), and HEC modified with a long-chain alkyl group, generically termed HMHEC (where HM = Hydrophobically Modified), manufactured by Aqualon Co. and sold under the trade name Natrosol Plus (39). These products are water-soluble. An organo-soluble ethyl modification is also available, which is classified as a derivative of ethylcellulose.

Water-soluble EHEC is a moderate ethyl DS ($\sim$1.0) modification of high hydroxyethyl MS ($\geq$2.0) HEC. Ethyl groups lower the surface and interfacial tensions, thereby increasing surface activity. This group also modifies adsorption properties of the polymer to particulates found in many formulations such as clays, pigments, and latices. Aqueous solutions have pseudoplastic rheology. High viscosity grades are more pseudoplastic than low viscosity materials, which approach Newtonian flow behavior. Viscosities decrease reversibly with increasing temperature. Above 65°C, EHEC precipitates from solution. Salts lower the temperature at which precipitation occurs. Solution viscosities are insensitive to pH between about 3 to 11. Aqueous solutions are miscible with lower alcohols, glycols, and ketones up to equal proportions. Water-soluble EHECs are used to thicken and stabilize a variety of materials, including water-borne paints, plasters, detergents, cosmetics, and pharmaceuticals (49).

HMHEC is a modification with low levels of much longer hydrocarbon chains (hydrophobes) that not only increase surface activity but also impart associative behavior to HEC; this produces dramatic effects on solution viscosity and rheology (37,74). For example, a HEC with a 2% solution viscosity of 10 $\text{mPa}\cdot\text{s}(=\text{cP})$ modified with $\sim$2.5 wt % of a C_{14}-chain hydrocarbyl moiety has a viscosity of 800 $\text{mPa}\cdot\text{s}(=\text{cP})$. The effect has been attributed to micellar aggregation of the hydrophobic groups in solution (37–39). The solubility and rheological properties of HMHEC depend primarily on the molecular weight, the DS and chain length of the hydrophobe, the polymer concentration, and the composition of the aqueous media. It has been found that HMHEC is an efficient rheology control agent in latex paints (39,74). Typical properties of a HMHEC are given in Table 7.

2.3. Methylcellulose and its Mixed Ethers.

Properties. Methylcellulose [9004-67-5] (MC) and its alkylene oxide derivatives hydroxypropylmethylcellulose [9004-65-3] (HPMC), hydroxyethylmethylcellulose [9032-42-2] (HEMC), and hydroxybutylmethylcellulose [9041-56-9] (HBMC) are nonionic, surface-active, water-soluble polymers. Each type of derivative is available in a range of methyl and hydroxyalkyl substitutions. The extent and uniformity of the methyl substitution and the specific type of hydroxyalkyl substituent affect the solubility, surface activity, thermal gelation, and other properties of the polymers in solution.

These four methylcelluloses are available in a range of substitutions.

	Methyl DS	Hydroxyalkyl MS
methylcellulose	1.4–2.0	
hydroxypropylmethylcellulose	1.1–2.0	0.1–1.0
hydroxyethylmethylcellulose	1.3–2.2	0.06–0.5
hydroxybutylmethylcellulose	≥1.9	≥0.04

Methylcellulose with a methyl DS less than about 0.6 is alkali-soluble. From about 1.6 to 2.4, it is water-soluble (most commercial grades); above 2.4, it is soluble in a wide variety of organic solvents. Methylcellulose solutions in water start to gel at ~55°C, independent of molecular weight. The gelation is a function of the DS, rate of heating, and type and amounts of additives such as salts. As the temperature increases, the viscosity initially decreases (typical behavior). When the gelling temperature is reached, the viscosity sharply rises until the flocculation temperature is reached. Above this temperature, the viscosity collapses. This process is reversible with temperature (75).

The mixed derivatives HEMC, HPMC, and HBMC tend to precipitate rather than gel as the temperature is increased. The higher the hydroxyalkyl substitution, the greater the tendency for precipitation. HEMCs and HPMCs tend to have higher gelation and flocculation temperatures (75). The mixed derivatives are generally more tolerant of added salts than methylcellulose itself. HPMC and HBMC are tolerant of and are soluble in some organic solvents, especially lower alcohols and glycols.

Solutions of methylcelluloses are pseudoplastic below the gel point and approach Newtonian flow behavior at low shear rates. Above the gel point, solutions are very thixotropic because of the formation of three-dimensional gel structure. Solutions are stable between pH 3 and 11; pH extremes will cause irreversible degradation. The high substitution levels of most methylcelluloses result in relatively good resistance to enzymatic degradation (16).

Methylcellulose and its mixed ethers are surface-active cellulose ethers having surface tension values as low as 44 mN/m(= dyn/cm) and interfacial tension values as low as 17 mN/m(= dyn/cm) against paraffin oil.

Typical properties of MC, HPMC, HEMC, and HBMC are given in Table 8.

Manufacture. Methylcellulose is manufactured by the reaction of alkali cellulose with methyl chloride (76).

$$R_{cell}OH : NaOH + CH_3Cl \longrightarrow R_{cell}OCH_3 + NaCl$$

The reaction is accompanied by side reactions that lead to methanol and dimethyl ether by-products.

$$CH_3Cl + NaOH \longrightarrow CH_3OH + NaCl$$

$$CH_3OH + CH_3Cl + NaOH \longrightarrow CH_3OCH_3 + NaCl + H_2O$$

Table 8. **Typical Properties of Methylcellulose Ethers**[a]

Property	MC	HPMC	HEMC	HBMC
	Powder			
appearance	white	white	white	white
bulk density, g/cm^3		0.25–0.70		
volatiles, %		8 max		
ash content (as Na_2SO_4), %		2.5 max		
	Solution			
viscosity[b], mPa · s(=cP)	10–15,000	5–70,000	100–70,000	
sp gr, 2% at 20°C		1.0032		
pH, 1%		5.5–9.5		
surface tension, 0.1%, mN/m(= dyn/cm)	47–53	44–56	46–53	49–55
interfacial tension[c], mN/m(= dyn/cm)	19–23	17–30	17–21	20–22
gelation temp, °C	48	54–70		49
flocculation temp, °C	50–75	60–90	60–90	
	Film			
tensile strength, MPa[d], 50% rh	58.6–78.6	58.6–61		
elongation, %, 50% rh	10–15	5–10		
softening point, °C		240		
melting point, °C	290–305	260		
vapor transmission, nmol/(m · s)[e]				
water, 37°C, 90–100% rh		520		
oxygen, 24°C		560		

[a] Refs. 42,43.

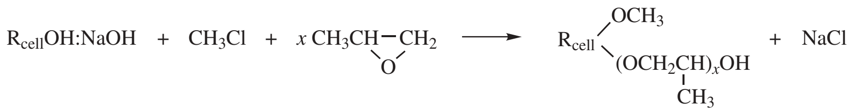
[b] 2% Solution, Brookfield, 20 rpm.

[c] Against paraffin oil.

[d] To convert MPa to psi, multiply by 145.

[e] To convert nmol/(m · s) to g · mil/100 in.^{2} · d for water, multiply by 3.95; for O_2, by 7.02.

Hydroxyalkyl modification is made by simultaneous or staged addition of an alkylene oxide, as exemplified in the following (77–79).



$$R_{cell}OH{:}NaOH + CH_3Cl + x\,CH_3CH\overset{O}{-}CH_2 \longrightarrow R_{cell}\begin{cases}OCH_3\\(OCH_2\underset{CH_3}{CH})_xOH\end{cases} + NaCl$$

Similarly, ethylene oxide and 1,2-butylene oxide are used to make methylhydroxy-ethylcellulose and methylhydroxybutylcellulose, respectively.

Unlike HEC and CMC, which are purified by washing with aqueous organic solvents, methylcellulose and its hydroxyalkyl modifications are purified in hot water where they are insoluble. As with other cellulose ethers, drying and grinding complete the process.

Economic Aspects. A breakdown of salient figures in 1987 for the methylcelluloses is given in Table 9. The Dow Chemical Company is the only U.S. manufacturer. They produce and market methyl- (MC), hydroxypropylmethyl-(HPMC), and hydroxybutylmethyl- (HBMC) celluloses. European producers include Aqualon Co. in Germany and Belgium, Hoechst AG in Germany,

Table 9. **Worldwide Supply and Demand for Methylcelluloses[a], 10^3t**

Region	Capacity	Production	Consumption	Imports	Exports
United States	22	16	16	1	2
Western Europe	51	44	35.5		
Japan	7	7	5		2
Canada, Latin America, other Asia					
Total	*80*	*67*	*62*		

[a] In 1987 (1).

Dow Chemical GmbH in Germany, Wolff Walsrode AG in Germany, and Courtaulds Fibres Ltd. in the United Kingdom. Shin-Etsu Chemical Co., Ltd. and Matsumoto Yushi-Seiyaku Co., Ltd. are the two Japanese manufacturers.

Specifications and Standards; Test Methods. Premium grades of methylcellulose meet the requirements of U.S.P. XIX and *Food Chemicals Codex II*, and the *International Codex Alimentarius*. They are GRAS, meeting the requirements of Food Additives Regulation 182.1480 as multiple purpose food substances for nonstandardized foods. Premium grades of some hydroxypropylmethylcelluloses meet requirements of U.S.P. XIX, *Food Chemicals Codex II*, and Food Additives Regulation 172.874, which allows their use in nonstandardized foods. Methylcellulose and hydroxypropylmethylcellulose qualify as inert ingredients under CRF 180.1000 that may be used in formulations applied to growing crops or raw agricultural commodities after harvest.

Analytical procedures and test methods are described in manufacturers' technical bulletins (42,43).

Uses. There are numerous applications for methylcellulose and its derivatives. Some important ones are summarized in Table 10.

2.4. Ethylcellulose and Hydroxyethylethylcellulose.

Properties. Ethyl cellulose [9004-57-3] (EC) is a nonionic, organo-soluble, thermoplastic cellulose ether, having an ethyl DS in the range of $\sim 2.2 - 2.7$. Actually, EC is water-soluble at DS ~ 1.2, but only those products that are thermoplastic and soluble in organic solvents are of commercial importance, because of their ability

Table 10. **Applications for Methylcellulose and its Derivatives[a]**

Industry	Application	Function
construction	cements, mortars	thickener, water-binder, workability
foods	mayonnaise, dressing	stabilizer, emulsifier
	desserts	thickener
pharmaceuticals	tablets	binder, granulation aid
	formulations	stabilizer, emulsifier
adhesives	wallpaper paste	adhesive
ceramics	slip casts	binder (promotes green strength)
coatings	latex paints	thickener
	paint removers	thickener
cosmetics	creams, lotions	stabilizer, thickener

[a] Refs. 42,43.

to form tough, stable films. Above a DS of about 2.5, EC is soluble in many nonpolar solvents.

Film mechanical properties, such as tensile strength, elongation, and flexibility, depend more on the molecular weight (degree of polymerization) than on substitution. Elongation and tensile strength increase to a maximum with increasing molecular weight; flexibility increases linearly.

Ethylcellulose is subject to oxidative degradation in the presence of sun- or ultraviolet light, especially at elevated temperatures above the softening point. It must, therefore, be stabilized with antioxidants (44). EC is stable to concentrated alkali and brines but is sensitive to acids.

Organo-soluble hydroxyethylethylcellulose (HEEC) is highly ethoxylated with small amounts of hydroxyethyl substitution. It is used in coating applications that require solubility in fast-drying aliphatic hydrocarbons. These EHEC polymers are the only commercially available cellulosic polymers substantially soluble in low cost, low odor aliphatic hydrocarbon solvents. As a result, formulation costs are lowered and application conditions are simplified. Like ethylcellulose, HEEC is subject to oxidative degradation by the combination of heat and light (45). Degradation is more rapid above the melting point (175°C). An antioxidant, such as octylphenol, combined with an acid acceptor, such as an epoxy resin, provides protection against heat degradation. Benzophenone derivatives provide protection against sunlight. Primary uses for organic solvent-soluble EHECs are as additives in printing inks, clear lacquers, and other coatings such as alkyd, flat, and semigloss finishes. Table 11 gives typical properties for EC and HEEC.

Manufacture. Ethyl chloride undergoes reaction with alkali cellulose in high pressure nickel-clad autoclaves. A large excess of sodium hydroxide and ethyl chloride and high reaction temperatures (up to 140°C) are needed to drive the reaction to the desired high DS values ($\geq$2.0). In the absence of a diluent, reaction efficiencies in ethyl chloride range between 20 and 30%, the

Table 11. **Typical Properties of EC and HEEC**[a]

Property	EC	HEEC
Powder		
appearance	white	white
volatiles, %	2	
bulk density, g/cm^3	0.3–0.35	0.3–0.35
softening point, °C	152–162	
Film		
specific gravity	1.140	1.120
refractive index	1.470	1.47
tensile strength, MPa[b]	46–72	34–41
elongation, %	7–30	6–10
flexibility[c]	160–2000	500–900
dielectric constant, 60 Hz	2.5–4.0	

[a] Refs. 44,46.

[b] To convert mPa to psi, multiply by 145.

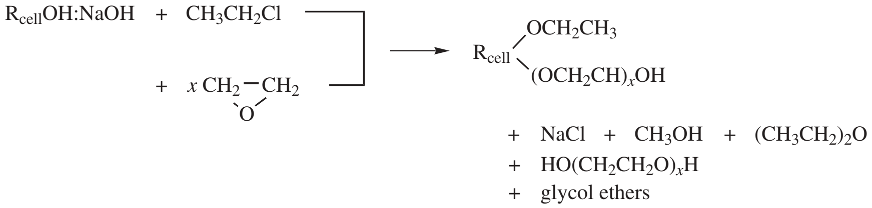
[c] MIT double folds.

majority of the rest being consumed to ethanol and diethyl ether by-products.

$$R_{\mathrm{cell}}OH : NaOH + CH_3CH_2Cl \longrightarrow R_{\mathrm{cell}}OCH_2CH_3 + NaCl + CH_3CH_2OH + (CH_3CH_2)_2O$$

Higher ethyl chloride efficiency is claimed for a process utilizing a hydrocarbon diluent coupled with stepwise addition of sodium hydroxide (80). Product work-up includes distillation to remove residual unreacted ethyl chloride, added diluent, methanol, and diethyl ether; neutralization of excess sodium hydroxide; washing in water to remove salts; drying; and grinding.

The manufacturing process for organo-soluble EHEC is similar to that for EC except that alkali cellulose reacts first with ethylene oxide to a low hydroxyethyl MS value of ~0.5 at a low temperature, ~50°C, followed by reaction of the ethyl chloride at a higher temperature. Additional by-products, which are removed during purification, include glycols and the reaction products of the glycols with ethyl chloride (glycol ethers).



Economic Aspects. The Dow Chemical Company and Aqualon Co. are the only listed principal producers of EC and HEEC products worldwide. Consumption has remained constant over the past several years, and the products are not expected to grow in the future. Production is estimated at 5000 t/yr, roughly equally divided between The Dow Chemical Company and Aqualon Co. As with other cellulose ethers, the price for EC and HEEC varies by grade.

Specifications and Standards; Test Methods. Ethylcellulose is cleared for many applications in food and food contact under the Federal Food, Drug, and Cosmetic Act, as amended. Examples include binder in dry vitamin preparations for animal feed, coatings and inks for paper and paperboard products used in food packaging, and closures with sealing gaskets for food containers (44). Methods of analyses are given in ASTM D914-72 (19), *National Formulary XIV*, and *Food Chemicals Codex II*.

Uses. A summary of the applications for ethylcellulose is given in Table 12.

Table 12. **Applications for EC and HEEC**[a]

Industry	Application	Function
coatings	lacquers, varnishes	protective film-former, additive to increase film toughness and durability, shorten drying time
printing	inks	film-former
adhesives	hot melts	additive to increase toughness

[a] Refs. 44,46.

2.5. Hydroxypropylcellulose. *Properties.* Hydroxypropylcellulose [9004-64-2] (HPC) is a thermoplastic, nonionic cellulose ether that is soluble in water and in many organic solvents. HPC combines organic solvent solubility, thermoplasticity, and surface activity with the aqueous thickening and stabilizing properties characteristic of other water-soluble cellulosic polymers described herein. Like the methylcelluloses, HPC exhibits a low critical solution temperature in water.

The substitution of HPC is defined by the MS. Molar substitutions higher than approximately 3.5 are needed for solubility in water and organic solvents.

HPC is available in a number of viscosity grades, ranging from about 3000 mPa · s(=cP) at 1% total solids in water to 150 mPa · s(=cP) at 10% total solids. HPC solutions are pseudoplastic and exceptionally smooth, exhibiting little or no structure or thixotropy. The viscosity of water solutions is not affected by changes in pH over the range of 2 to 11. Viscosities decrease as temperature is increased. HPC precipitates from water at temperatures between 40 and 45°C. Dissolved salts and other compounds can profoundly influence the precipitation temperature (50,81).

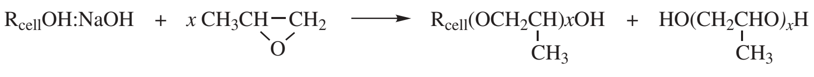
HPC is compatible with many natural and synthetic water-soluble polymers and gums (50). Generally, blends of HPC with another nonionic polymer such as HEC yield water solutions having viscosities in agreement with the calculated value. Blends of HPC and anionic CMC, however, produce solution viscosities greater than calculated. This synergistic effect may be reduced in the presence of dissolved salts or if the pH is below 3 or above 10.

Like the methylcelluloses, water solutions of HPC display greatly reduced surface tension. A 0.1% solution of HPC at 25°C has a surface tension of about 44 mN/m(=dyn/cm) (water is 74.1 mN/m) and interfacial tension of about 12.5 mN/m(=dyn/cm) against mineral oil. The molecular weight of the HPC has only a slight effect on the surface tension.

Examples of polar organic solvents that dissolve HPC are methanol, ethanol, propylene glycol, and chloroform. There is no tendency for HPC to precipitate as the temperature is raised. In fact, elevated temperatures improve the solvent power of organic liquids.

Some typical properties of commercial HPC are given in Table 13.

Manufacture. HPC is manufactured by reaction of propylene oxide [75-56-9] with alkali cellulose.



$$R_{cell}OH{:}NaOH + x\,CH_3\underset{\diagdown O \diagup}{CH-CH_2} \longrightarrow R_{cell}(OCH_2\underset{CH_3}{\underset{|}{C}}H)xOH + HO(CH_2\underset{CH_3}{\underset{|}{C}}HO)_xH$$

The reaction may be conducted in stirred autoclaves in the presence of hydrocarbon diluents (82,83). Like the methylcelluloses, advantage is taken of the low critical solution temperature of HPC and it is purified through multiple washings with hot water. Consequently, very low levels of residual salts and by-products are present in the final products.

Economic Aspects. The Aqualon Co. is the only U.S. manufacturer. It is also produced in Japan by Nippon Soda Co., Ltd. Worldwide consumption in 1987 was estimated at 2300 metric tons.

Table 13. **Typical Properties of HPC**[a]

Property	Value
Powder	
appearance	off-white
volatiles, %	5 max
ash content (as Na_2SO_4), %	0.2–0.5
softening point, °C	100–150
molecular weight, M_w	$8.0 \times 10^4 - 1.15 \times 10^6$
Solution	
viscosity, Brookfield, 30 rpm, mPa · s(=cP)	
at 1% (high M_w)	2500
at 10% (low M_w)	100
surface tension, 0.1%, mN/m(=dyn/cm)	43.6
interfacial tension[b], 0.1%, mN/m	12.5
Film	
tensile strength, MPa[c]	14
elongation, %	50
flexibility[d] (50 μm film)	10,000
refractive index	1.559

[a] Ref. 50.

[b] Against mineral oil.

[c] To convert MPa to psi, multiply by 145.

[d] MIT double folds.

Specifications and Standards; Test Methods. Food-grade HPC products are manufactured for use in food and conform to the specifications for HPC set forth in CFR 21, Section 172.870. Food grades of HPC also conform to the specifications for HPC as listed in the current edition of the *Food Chemicals Codex*.

Pharmaceutical and cosmetic grades of HPC, as for example Klucel NF manufactured by Aqualon Co., conform to the requirements of the HPC monograph as listed in the current edition of the *National Formulary*.

Toxicity testing indicates that HPC is physiologically inert (50).

Procedures for determining the ash content and moisture level, solution preparation, and viscosity measurement techniques are given in the manufacturer's literature (50).

Uses. A summary of significant uses for HPC is given in Table 14.

Table 14. **Applications for HPC**[a]

Industry	Application	Function
polymerization	PVC suspension polymerization	protective colloid
pharmaceutical	tablets	binder, film-former
coatings	paint remover	thickener
foods	whipped toppings	stabilizer
	processed foods	extrusion aid
ceramics	slip casts	binder (promotes green strength)

[a] Ref. 50.

BIBLIOGRAPHY

"Cellulose Derivatives" in *ECT* 1st ed., Vol. 3, pp. 357–391; and in *ECT* 2nd ed., Vol. 4, pp. 616–652 both by E. D. Klug, Hercules Powder Company; "Cellulose Derivatives, Ethers" in *ECT* 3rd ed., Vol. 5, p. 143–163 by G. K. Greminger, Jr., Dow Chemical U.S.A.

CITED PUBLICATIONS

1. *Chemical Economics Handbook*, SRI International, Menlo Park, Calif., 1989, Section 581.5000A.
2. J. O. Warwicker, R. Jeffries, R. L. Colbran, and R. N. Robinson, *A Review of the Literature on the Effect of Caustic Soda and Other Swelling Agents on the Fine Structure of Cotton*, Shirley Institute Pamphlet No. 93, Shirley Institute, Didsbury, Manchester, UK, 1966.
3. T. Okano and A. Sarko, *J. Appl. Polym. Sci.* **29**, 4175–4182 (1984).
4. T. Okano and A. Sarko, *J. Appl. Polym. Sci.* **30**, 325–332 (1985).
5. H. Nishimura and A. Sarko, *J. Appl. Polym. Sci.* **33**, 855–866 (1987).
6. H. Nishimura and A. Sarko, *J. Appl. Polym. Sci.* **33**, 867–874 (1987).
7. D. Entwistle, E. H. Cole, and N. S. Wooding, *Text. Res. J.* **XIX**(9), 527–624 (1949).
8. R. I. C. Michie and S. M. Neale, *J. Polym. Sci. Part A* **2**, 2063–2083 (1964).
9. U.S. Pat. 2,512,338 (June 20, 1950), E. D. Klug and H. M. Spurlin (to Hercules Powder Co.).
10. U.S. Pat. 3,719,663 (Mar. 6, 1973), E. D. Klug (to Hercules Inc.).
11. U.S. Pat. 3,728,331 (Apr. 17, 1973), A. B. Savage (to The Dow Chemical Company).
12. U.S. Pat. 4,061,859 (Dec. 6, 1977), W-J. Cheng (to The Dow Chemical Company).
13. U.S. Pat. 3,391,135 (July 2, 1968), S. Ouno and co-workers (to Shin-Etsu Chemical Industry Co., Ltd.).
14. *Aqualon*^{TM} *Cellulose Gum, Sodium Carboxymethylcellulose, Physical and Chemical Properties*, Aqualon Co., a Hercules Incorporated Company, Wilmington, Del., 1988.
15. D. J. Sikkema and H. Janssen, *Macromolecules* **22**, 364–366 (1989).
16. M. G. Wirick, *J. Polym. Sci. Part A-1* **6**, 1705–1718 (1968).
17. J. E. Glass, A. M. Buettner, R. G. Lowther, C. S. Young, and L. A. Cosby, *Carbohydr. Res.* **84**, 245–263 (1980).
18. U.S. Pat. 4,401,813 (Aug. 30, 1983), J. L. Lowell, M. J. Nevins, K. L. G. Reid, and K. L. Walter (to NL Industries, Inc.).
19. U.S. Pat. 4,525,585 (June 25, 1985), A. Taguchi and T. Ohmiya (to Diacel Chemical Industries, Ltd.).
20. S-I. Takahashi, T. Fujimoto, T. Miyamoto, and H. Inagaki, *J. Polym. Sci.: Part A* **25**, 987–994 (1987).
21. J. Reuben and H. T. Conner, *Carbohydr. Res.* **115**, 1–13 (1983).
22. J. Reuben, *Carbohydr. Res.* **157**, 201–213 (1986).
23. J. Reuben, *Carbohydr. Res.* **161**, 23–30 (1987).
24. J. Reuben and T. E. Casti, *Carbohydr. Res.* **163**, 91–98 (1987).
25. J. R. DeMember and co-workers, *J. Appl. Polym. Sci.* **21**, 621–627 (1977).
26. A. Parfondry and A. S. Perlin, *Carbohydr. Res.* **57**, 39–49 (1977).
27. Y. Tezuka, K. Imai, M. Oshima, and T. Chiba, *Polymer* **30**, 2288–2291 (1989).
28. B. Lindberg, U. Linquist, and O. Stenberg, *Carbohydr. Res.* **170**, 207–214 (1987).
29. S. P. Rowland, in N. M. Bikales, ed., *Encyclopedia of Polymer Science and Technology*, 1st ed., Suppl. Vol. 1, Wiley-Interscience, New York, 1976, 146–175.
30. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 3rd ed., Section VII, John Wiley & Sons, Inc., 1989.

31. R. A. Gelman, *J. Appl. Polym. Sci.* **27**, 2957–2964 (1982).
32. R. A. Gelman and H. G. Barth, in J. E. Glass, ed., *Water-Soluble Polymers: Beauty with Performance, Advances In Chemistry Series No. 213*, American Chemical Society, Washington, D.C., 1986.
33. H. G. Barth, *J. Chromatogr. Sci.* **18**, 409–429 (1980).
34. E. Pfannkoch, K. C. Lu, F. E. Regnier, and H. G. Barth, *J. Chromatogr. Sci.* **18**, 430–441 (1980).
35. H. G. Barth and F. E. Regnier, *J. Chromatogr.* **192**, 275–293 (1980).
36. G. Holzwarth, L. Soni, and D. N. Schulz, *Macromolecules* **19**, 422–426 (1986).
37. L. M. Landoll, *J. Polym. Sci. Polym. Chem. Ed.* **20**, 443 (1982).
38. A. C. Sau and L. M. Landoll, in J. E. Glass, ed., *Polymers in Aqueous Media, Advances in Chemistry Series Vol. 223*, American Chemical Society, Washington, D.C., 1989, p. 343.
39. *Natrosol® Plus—Modified Hydroxyethylcellulose*, Aqualon Co., a Hercules Incorporated Company, Wilmington, Del., 1988.
40. *Natrosol® Hydroxyethylcellulose,* Physical and Chemical Properties, Aqualon Co., a Hercules Incorporated Company, Wilmington, Del., 1987.
41. *Cellosize® Hydroxyethylcellulose*, Union Carbide Corp., New York, 1981.
42. *Methocel®*, The Dow Chemical Company, Midland, Mich., 1978.
43. *Culminal® Methylcellulose, Physical and Chemical Properties*, Aqualon Co., a Hercules Incorporated Company, Wilmington, Del.
44. *Chemical and Physical Properties of Hercules® Ethylcellulose*, Hercules Inc., Wilmington, Del., 1982.
45. *Tough Ethocel® Ethyl Cellulose Resin*, The Dow Chemical Company, Midland, Mich., 1974.
46. *Chemical and Physical Properties of Hercules® EHEC Ethylhydroxyethylcellulose*, Hercules Inc., Wilmington, Del., 1981.
47. *Celquat®*, *Cationic Cellulosic Polymers For Cosmetics and Toiletries*, National Starch and Chemical Corp., Bridgewater, N.J.
48. *Polymer JR For Hair Care*, Union Carbide Corp., New York.
49. *Bermocoll® Cellulose Ethers*, Berol Kemi AB, Sweden, 1977.
50. *Klucel® Hydroxypropylcellulose, Physical and Chemical Properties*, Aqualon Co., a Hercules Incorporated Company, Wilmington, Del., 1987.
51. *National Fire Codes®: A Compilation of NFPA Codes, Standards, Recommended Practices, Manuals, and Guides*, Vol. II, National Fire Protection Association, Md., 1987.
52. U.S. Pat. 4,525,585 (June 25, 1985), A. Taguchi and T. Ohmiya (to Diacel Chemical Industries, Ltd.).
53. U.S. Pat. 2,517,577 (Aug. 8, 1950), E. D. Klug and J. S. Tinsley (to Hercules Powder Co.).
54. U.S. Pat. 2,976,278 (Mar. 21, 1961), O. H. Paddison and R. W. Somer (to E. I. du Pont de Nemours & Co., Inc.).
55. U.S. Pat. 4,460,766 (July 17, 1984), U-H Felcht and E. Perplies (to Hoechst Aktiengesellschaft).
56. U.S. Pat. 2,523,377 (Sept. 26, 1950), E. D. Klug (to Hercules Powder Co.).
57. U.S. Pat. 2,553,725 (May 22, 1951), L. N. Rogers, W. A. Mueller, and E. E. Hembree (to Buckeye Chemical Oil Co.).
58. R. N. Hadar, W. F. Waldeck, and F. W. Smith, *Ind. Eng. Chem.* **44**, 2803 (1952).
59. U.S. Pat. 2,879,268 (Mar. 24, 1959), E. I. Jullander (to Mo Och Domsjo Aktiebolag).
60. U.S. Pat. 3,072,635 (Jan. 8, 1963), J. H. Menkart and R. S. Allan (to Chemical Development of Canada).
61. U.S. Pat. 3,356,519 (Dec. 5, 1967), W. C. Chambers and M. Lee (to The Dow Chemical Company).

62. Can. Pat. 947,281 (May 14, 1974), W. Patten (Union Carbide Corp.).
63. U.S. Pat. 2,572,039 (Oct. 23, 1951), E. D. Klug and H. G. Tennent (to Hercules Powder Co.).
64. U.S. Pat. 2,682,535 (June 29, 1954), A. E. Broderick (to Union Carbide Corp.).
65. ASTM D2364-69, *Standard Methods for Testing Hydroxyethylcellulose*, American Society of Testing and Materials, Easton, Md.
66. U.S. Pat. 4,035,195 (July 12, 1977), T. J. Podlas (to Hercules Inc.).
67. U.S. Pat. 2,618,595 (Nov. 18, 1954), W. E. Gloor (to Hercules Powder Co.).
68. U.S. Pat. 3,284,353 (Nov. 18, 1966), J. B. Batdorf (to Hercules Powder Co.).
69. U.S. Pat. 4,433,731 (Feb. 28, 1984), J. Chatterji, B. G. Brake, and J. M. Tinsley (to Halliburton Co.).
70. U.S. Def. Publ. T103,401 (Sept. 6, 1983), T. G. Majewicz.
71. *Hercules CMHEC 37L, Technical Bulletin VC-402C*, Hercules Inc., Wilmington, Del.
72. U.S. Pat. 3,472,840 (Oct. 14, 1969), F. W. Stone and J. M. Rutherford, Jr. (to Union Carbide Corp.).
73. U.S. Pat. 4,464,523 (Aug. 7, 1984), D. Neigel and J. Kancylarz (to National Starch and Chemical Corp.).
74. U.S. Pat. 4,228,277 (Oct. 14, 1980), L. M. Landoll (to Hercules Inc.).
75. N. Sarkar, *J. Appl. Polym. Sci.* **24**, 1073–1087 (1979).
76. U.S. Pat. 4,117,223 (Sept. 26, 1978), W. Lodige, F. Lodige, J. Lucke, and E. Lipp.
77. U.S. Pat. 4,339,573 (July 13, 1982), W. Wust, H. Leischner, W. Rahse, F-J. Carduck, and N. Kune (to Henkel Kommanditgesellschaft Aktien).
78. U.S. Pat. 4,477,657 (Oct. 16, 1984), C. P. Strange, C. D. Messelt, and C. W. Gibson (to The Dow Chemical Company).
79. U.S. Pat. 4,456,751 (June 26, 1984), C. D. Messelt and G. P. Townsend (to The Dow Chemical Company).
80. U.S. Pat. 2,254,249 (Sept. 2, 1941), R. W. Swinehart and A. T. Maasberg (to The Dow Chemical Company).
81. E. D. Klug, *J. Polym. Sci.: Part C* **36**, 491–508 (1971).
82. U.S. Pat. 3,278,521 (Oct. 11, 1966), E. D. Klug (to Hercules Inc.).
83. U.S. Pat. 3,357,971 (Dec. 12, 1967), E. D. Klug (to Hercules Inc.).

GENERAL REFERENCES

E. K. Just and T. G. Majewicz, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. 3, John Wiley & Sons, Inc., New York, 1985, 224–269.

E. Ott, M. Spurlin, and M. W. Graffin, ed., *Cellulose and Cellulose Derivatives, High Polymers*, Vol. V, Wiley-Interscience, New York, 1954–1955, Parts I–III.

N. M. Bikales and L. Segal, eds., *Cellulose and Cellulose Derivatives, High Polymers*, Vol. V, Wiley-Interscience, New York, 1971, Pts. IV–V.

R. L. Davidson, ed., *Handbook of Water-Soluble Gums and Resins*, McGraw-Hill, New York, 1980.

J. E. Glass, ed., *Water-Soluble Polymers—Beauty With Performance: Advances in Chemistry Series No. 213*, American Chemical Society, Washington, D.C., 1986.

J. E. Glass, ed., *Polymers In Aqueous Media: Performance Through Association: Advances In Chemistry Series No. 223*, American Chemical Society, Washington, D.C., 1989.

THOMAS G. MAJEWICZ
THOMAS J. PODLAS
Aqualon Company