Dow



METHOCEL Cellulose Ethers

Technical Handbook





Contents

An Introduction to METHOCEL Cellulose Ethers
General Properties of METHOCEL Cellulose Ethers
Applications for METHOCEL Cellulose Ethers
Regulated Uses
How to Prepare Aqueous Solutions of METHOCEL Cellulose Ethers 11
How to Prepare Solutions of METHOCEL Cellulose Ethers in Nonaqueous Solvents and Nonsolvent Media
Properties of METHOCEL Cellulose Ethers in Powder Form
Properties of Solutions of METHOCEL Cellulose Ethers
Thermal Gelation in Aqueous Media22
Properties of Films of METHOCEL Cellulose Ethers
Analytical Methods
Handling Considerations

An Introduction to METHOCEL Cellulose Ethers

METHOCEL* cellulose ethers are water-soluble polymers derived from cellulose, the most abundant polymer in nature. For over 50 years these versatile products have played an important role in foods, cosmetics, pharmaceuticals, latex paints, construction products, ceramics, and a host of other applications.

METHOCEL products are used as thickeners, binders, film formers, and water-retention agents. They also function as suspension aids, surfactants, lubricants, protective colloids, and emulsifiers. In addition, solutions of METHOCEL thermally gel, a unique property that plays a key role in a surprising variety of applications. You won't find this valuable combination of properties in any other water-soluble polymer.

Multifunctionality and Efficiency Improve Formulation Economy

The fact that so many useful properties are simultaneously present and often act in combination can be a significant economic advantage. In many applications, two, three, or more ingredients would be required to do the same job performed by a single METHOCEL product. In addition, METHOCEL cellulose ethers are highly efficient, often yielding optimum performance at a lower concentration than that required with other water-soluble polymers.

Range of Products Offers Formulating Versatility

The broad range of METHOCEL products available is certainly one reason they've been used successfully in so many different applications. There are two different chemical types and each is available in different grades, physical forms, and viscosities. By choosing a specific METHOCEL product, it's possible

to obtain the optimum degree of thickening, binding, moisture retention, and other properties desired in a given formulation.

Premium and Food Grades for Food and Drug Applications

METHOCEL Premium and Food products have long been used by the food and drug industries. Both methylcellulose and hydroxypropyl methylcellulose are recognized as acceptable food additives by the U.S. Food and Drug Administration (FDA) and are listed in the Food Chemicals Codex and the International Codex Alimentarius. Both are included in the United States Pharmacopoeia (USP XXI). Methylcellulose is considered Generally Recognized As Safe (GRAS) by the FDA.

Standard Grades for Other Applications

Standard grade METHOCEL products have the same performance properties as Premium grades. The major difference is that Standard grades can have slightly higher levels of impurities. Standard grades are not approved for use in foods, although some Standard grade products may be used as components of containers coming in contact with food (indirect food additive).

Viscosity Grades from 3 to 100,000 mPa·s

METHOCEL cellulose ether products are available in various viscosity grades, ranging from 3 to over 200,000 mPa·s.† Because the viscosity of a solution depends on the concentration of METHOCEL, this wide range of product viscosity allows you to obtain the viscosity you want in a formulation, while using a concentration that gives the desired level of other performance properties.

Available as Powders, Surface-treated Powders, and in Granular Form

For further formulating versatility, METHOCEL products are available in three different forms: powder, surface-treated powder, and granular. The form influences the techniques used in making solutions. Untreated powders are soluble in cold water, but must be thoroughly dispersed before they begin to dissolve. Surface-treated powders and granular products can be added directly to aqueous systems. The dissolution of these products can be controlled by a shift in pH.

Techniques commonly used in preparing solutions with different physical forms of METHOCEL products are summarized on pages 11–14 of this handbook.

Key to Product Nomenclature for METHOCEL Products

METHOCEL is a trademark of The Dow Chemical Company for a line of cellulose ether products. An initial letter identifies the type of cellulose ether. "A" identifies methylcellulose products. "E", "F", "J", and "K" identify different hydroxypropyl methylcellulose products.

The number that follows identifies the viscosity in millipascal-seconds (mPa·s) of that product measured at 2% concentration in water at 20°C. In designating viscosity, the letter "C" is frequently used to represent 100 and the letter "M" is used to represent 1,000.

Several different suffixes are also used to identify special products. "P" is sometimes used to identify METHOCEL Premium grade products. "LV" refers to special "low viscosity" products. "G" identifies "granular" products. The letter "S" identifies

^{*} Trademark of The Dow Chemical Company

[†] Note: mPa·s (millipascal-seconds) is equivalent to centipoise. All solution viscosities are measured with Ubbelohde viscometers at 2% concentration in water at 20°C (68°F).

"surface-treated" products, "CR" denotes a controlled-release grade, and "FG" identifies food grade. Developmental grades are denoted by the letter X plus a second letter (usually U or Y) plus a five-digit code.

There are also a number of specialpurpose METHOCEL products developed for cosmetics, pharmaceuticals, ceramics, and other applications which have different systems of nomenclature. For example, METHOCEL 40-Series products make up a family of special surface-treated products for cosmetic formulations.

Example A: METHOCEL A4C Premium is the designation for a Premium grade methylcellulose product having a viscosity of 400 mPa·s.

Example B: METHOCEL J5MS is a Standard grade hydroxypropyl methylcellulose product with a viscosity of 5,000 mPa·s, which has been surface-treated for easy dispersion.

How to Get Started Formulating with METHOCEL

To completely evaluate how METHOCEL cellulose ethers can improve quality, performance, and economy in your formulations, you'll want to try them in your own lab. Whether you are developing an entirely new product or working to improve an existing one, chances are you'll find a METHOCEL product that's ideally suited to your needs.

Free Samples and Literature Available

Sample quantities of METHOCEL products are available free of charge for your developmental work. You can obtain samples by calling one of the numbers listed on the back cover of this brochure. Literature covering the use of METHOCEL products in many of the applications listed on pages 7–9 of this handbook is also available on request. Just tell us what types of formulations or products you are evaluating, and we'll send you all the current literature that applies. Or visit our website at www.methocel.com for a complete selection of downloadable literature.

Our Technical Service and Development Staff Can Help

Talking with someone on our Technical Service and Development (TS&D) staff can save you a great deal of formulation time. In certain applications, a blend of METHOCEL products may give the best results, and the details may have already been worked out by someone in our lab. We have technical personnel who specialize in foods, ceramics, paints, cosmetics, pharmaceuticals, construction products, and other specific uses for METHOCEL products. By taking advantage of their experience with METHOCEL, you'll get a head start with your formulation and be certain of getting the most out of these versatile products.

Contact Us Today!

Again, if you would like samples, additional literature, or technical assistance, don't hesitate to call. Our numbers are listed on the back cover of this brochure. Call today. The sooner you get started formulating with METHOCEL, the sooner you'll start seeing improved performance and economy in your products. Our website also contains valuable information to assist you in learning more about METHOCEL.

General Properties of METHOCEL Cellulose Ethers

General properties common to the whole family of METHOCEL cellulose ether products are listed below. Individual METHOCEL products exhibit these properties to varying degrees and may have additional properties that are desirable for specific applications. Detailed information on the performance properties of METHOCEL products can be found on pages 15–21.

Water solubility. METHOCEL cellulose ethers dissolve in water with no sharp solubility limit. Surface-treated and granular METHOCEL products can be added directly to aqueous systems. This feature provides exceptional handling flexibility and control of solubilization rate. Although untreated METHOCEL powders are soluble in cold water, they must first be thoroughly dispersed in the water to prevent lumping. Dispersion techniques are described on pages 11–13. The maximum concentration is limited only by solution viscosity.

Organic solubility. Certain types and grades of METHOCEL cellulose ethers are also soluble in binary organic and organic solvent/water systems, providing a unique combination of organic solubility and water solubility.

No ionic charge. METHOCEL cellulose ethers are nonionic and will not complex with metallic salts or other ionic species to form insoluble precipitates.

Thermal gelation. Aqueous solutions of METHOCEL products gel when heated above a particular temperature, providing controllable quick-set properties. Unlike gels formed by protein thickeners, the gels go back into solution upon cooling.

Surface activity. METHOCEL products act as surfactants in aqueous solutions to provide emulsification, protective colloid action, and phase stabilization. Surface tensions range from 42 to 64 mN/m. The surface tension of water is 72 mN/m; a typical surfactant has a surface tension of 30 mN/m.

Metabolic inertness. Used as food and drug additives, METHOCEL products do not add calories to the diet.

Enzyme resistance. Enzymeresistant METHOCEL products provide excellent viscosity stability during long-term storage.

Low taste and odor. METHOCEL cellulose ethers have excellent (low) flavor and aroma properties, which is important in food and pharmaceutical applications.

pH stability. METHOCEL cellulose ethers are stable over a pH range of 2.0 to 13.0.

Water retention. METHOCEL cellulose ethers are highly efficient water-retention agents. This is valuable in food products, ceramics, coatings on adsorbent construction substrates, and many other applications.

Thickening. METHOCEL cellulose ethers thicken both aqueous and nonaqueous systems. The viscosity is related to the molecular weight, chemical type, and concentration of the specific METHOCEL product.

Film formation. METHOCEL products form clear, tough, flexible films that are excellent barriers to oils and greases. In food applications, this property is often

used to retain moisture and prevent oil absorption during cooking.

Binding. METHOCEL cellulose ethers are used as high-performance binders for pigments, paper, tobacco products, structured foods, pharmaceutical products, and ceramics.

Lubrication. METHOCEL products are used to reduce friction in rubber, cement, and ceramic extrusions. They are also used to improve pumpability of concrete and spray plasters, such as stucco, and in food applications as lubricity aids in extrusion and other forming processes.

Suspending. METHOCEL products are used to control settling of solid particles, for example, herbs and spices in salad dressings, solids in ceramic slips, and antacid suspensions.

Protective colloidal action.

METHOCEL products are used to prevent droplets and particles from coalescing or agglomerating.

Emulsification. METHOCEL cellulose ethers stabilize emulsions by reducing surface and interfacial tensions and by thickening the aqueous phase.

Nonaqueous Solvent Solubility

In general, binary solvent systems function more effectively with METHOCEL products than single solvents. Where alcohols comprise part of the binary solvent, solubility improves as the molecular weight of the alcohol decreases. Table 1 lists several compounds which are typical of the types of solvents that can be used with certain METHOCEL cellulose ether products.

Table 1: Typical Nonaqueous Solvents Used with METHOCEL Cellulose Ethers

- Furfuryl alcohol
- Dimethyl formamide
- Dimethyl sulfoxide
- Methyl salicylate
- Propylene carbonate
- Formic acid
- Glacial acetic acid
- Pvridine
- Mixtures of methylene chloride and ethyl, methyl, or isopropyl alcohols
- Mixtures of chloroform and methanol or ethanol
- N-Methyl pyrrolidone

Table 2: Representative Solvents for METHOCEL E and METHOCEL J Cellulose Ether Products at Elevated Temperatures

Solvent	Boiling Point °C	Solubility Point °C	Degree of Solubility ^a
Glycols			
Ethylene glycol	197.3	158	C
Diethylene glycol	244.8	135	C
Propylene glycol	188.2	140	C
1,3-Propanediol	214	120	C
Glycerine	290	260	P
DOWANOL* EE ethylene	134.7	120	C
glycol, ethyl ether			
DOWANOL TPM	242.4	160	P
tripropylene glycol, methyl ether			
Esters			
Ethyl glycolate	160	110	С
Glyceryl monoacetate (Acetin)	127	100	С
at 4 mbar			
Glyceryl diacetate (Diacetin)	123-133	100	C
at 5 mbar			
Amines			
Monoethanolamine	170–172	120	C
Diethanolamine	268–269	180	С

^{*} Trademark of The Dow Chemical Company

Solvent Solubility at Elevated Temperatures

METHOCEL E and METHOCEL J cellulose ether products possess structures that provide unusual solubility properties. They are soluble in certain nonaqueous media at elevated temperatures, permitting the formulation of mixes which can be fabricated by techniques of extrusion, hot-melt casting, and injection and compression molding. Examples of suitable "hot solvents" are found in Table 2.

METHOCEL 310 Series Products

METHOCEL 310 Series products are granular, high-viscosity materials (Table 3) that are sold only in Europe at this time. Controlled granulometry provides good dryflow properties, low dust formation, and lump-free dispersibility in water as well as organic solvents. Their carefully balanced level of substitution renders them soluble in both water and certain organic solvents or blends of solvents (Table 4). METHOCEL 310 cellulose ether products can be added directly to any solvent or blend of solvents under normal agitation. When using solvent blends there is no need to pre-disperse the product in a non-solvent or lowsolvent component.

^a C= completely soluble; P= partially soluble

Table 3: Typical Properties for METHOCEL 310 Cellulose Ether

Physical Form	Slightly off-white granules		
Nominal viscosity 1% Brookfield RVT, RT, 20 rpm	Solvent Type in methanol (MeOH) in ethanol (EtOH) in methylene chloride (MeCl ₂)	after 1 hour 500 mPa·s 600 mPa·s 7,500 mPa·s	after 24 hours 650 mPa·s 900 mPa·s 10,000 mPa·s
Moisture (as packaged)	max. 8%		
Sodium chloride	max. 1.5%		
Particle size	ca. 100-500 micron		

Table 4: Some Typical Solvents and Solvent Blends for METHOCEL 310 Cellulose Ether

		Solution Appearance				
Solvents	Clear, Smooth	Hazy, Structured	Swellable	Insoluble		
Ethanol (EtOH)		•				
Methanol (MeOH)		•				
Ethanol/H ₂ O 40/60	•					
Methanol/H ₂ O 40/60	•					
Methylene chloride (MeCl ₂)		•				
MeCl ₂ /EtOH 84/16	•					
MeCl ₂ /MeOH 84/16	•					
Tetrahydrofuran (THF)			•			
THF/H ₂ O 90/10-80/20	•					
Isopropanol				•		
Isopropanol/H ₂ O 90/10-60/40	•					
Isopropanol/MeCl ₂	•					
1,1,1-Trichloroethane				•		
Polypropylene glycol				•		
Polypropylene glycol/H ₂ O 70/30		e delayed thickening				
Butylglycol				•		
Butylglycol/H ₂ O 50/50	•					
Dioxane		•		•		
Acetone			•			
CELLOSOLVE™			•			
Dimethylformamide	•					
DOWANOL PM	•	•				

Chemistry of METHOCEL Cellulose Ethers

METHOCEL cellulose ether products are available in two basic types: methylcellulose and hydroxypropyl methylcellulose. Both types of METHOCEL have the polymeric backbone of cellulose, a natural carbohydrate that contains a basic repeating structure of anhydroglucose units (Figure 1). During the manufacture of cellulose ethers, cellulose fibers are heated with a caustic solution which in turn is treated with methyl chloride, yielding the methyl ether of cellulose. The fibrous reaction product is purified and ground to a fine, uniform powder.

Methylcellulose is made using only methyl chloride. These are METHOCEL A brand products. For hydroxypropyl methylcellulose products (METHOCEL E, F, J, and K brand products), propylene oxide is used in addition to methyl chloride to obtain hydroxypropyl substitution on the anhydroglucose units. This substituent group, -OCH₂CH(OH)CH₃-, contains a secondary hydroxyl on the number two carbon and may also be considered to form a propylene glycol ether of cellulose. These products possess varying ratios of hydroxypropyl and methyl substitution, a factor which influences organic solubility and the thermal gelation temperature of aqueous solutions.

There are also special-grade METHOCEL products available that have been formulated to meet the requirements of specific industries.

Degree of Substitution

The amount of substituent groups on the anhydroglucose units of cellulose can be designated by weight percent or by the average number of substituent groups attached to the ring, a concept known to cellulose chemists as "degree of substitution" (D.S.).

Figure 1: Typical Chemical Structures of METHOCEL Products

If all three available positions on each unit are substituted, the D.S. is designated as 3; if an average of two on each ring are reacted, the D.S. is designated as 2, etc.

The number of substituent groups on the ring determines the properties of the various products. METHOCEL A cellulose ether contains 27.5 to 31.5% methoxyl, or a methoxyl D.S. of 1.64 to 1.92, a range that yields maximum water solubility. A lower degree of substitution gives products having lower water solubility, leading to products that are only soluble in caustic solutions.

Higher degrees of substitution produce methylcellulose products that are soluble only in organic solvents.

In the METHOCEL E, METHOCEL F, and METHOCEL K cellulose ether products, the methoxyl substitution is still the major constituent (Table 5). The molar substitution (MS) reports the number of moles of hydroxypropyl groups per mole of anhydroglucose. In the METHOCEL J and 310-Series products, the hydroxypropyl substitution is about 50% of the total substitution.

Table 5: Degree of Substitution for METHOCEL Products

Product	Methoxyl Degree of Substitution	Methoxyl %	Hydroxypropyl Molar Substitution	Hydroxypropyl %
METHOCEL A	1.8	30	_	_
METHOCEL E	1.9	29	0.23	8.5
METHOCEL F	1.8	28	0.13	5.0
METHOCEL J	1.3	18	0.82	27
METHOCEL K	1.4	22	0.21	8.1
METHOCEL	2.0	25	0.8	25
310 Series				

Applications for METHOCEL Cellulose Ethers

The diverse products and processes listed here all have one thing in common: All benefit significantly from remarkably small concentrations of METHOCEL cellulose ethers. In most cases, the major benefits are improved physical properties, but in many applications there are improvements in processing efficiency and overall economy as well.

For more detailed information on any of these applications, contact one of the numbers listed on the back cover of this brochure or visit our website at www.methocel.com.

Adhesives

Carpet backsizing compounds.

METHOCEL products impart excellent foaming characteristics or "pan froth" to backsizing compounds. This helps keep the adhesive in the glue line instead of soaking into the backing materials. Also, due to thermal gelation, adhesives set quickly and dry faster at elevated temperatures.

Leather processing adhesives.

METHOCEL cellulose ethers are used to paste hides to smooth porcelain or glass surfaces in leather drying processes. Because of its water retention efficiency and thermal gelation, METHOCEL is much more effective than starchbased pastes.

Plywood laminating adhesives.

METHOCEL products are used in plywood laminating adhesives to control viscosity in glues for plywood manufacture. Thermal gelation and thickening properties of METHOCEL products keep the adhesive from soaking into the wood.

Cigar and cigarette adhesives.

Safe and efficient, METHOCEL products have long been used as binders for reconstituted tobacco sheets and as adhesives for cigar and cigarette manufacture.

Wallpaper pastes. Used as the primary adhesive in dry mixes, METHOCEL cellulose ether provides the wet tack required to hold a variety of paper types on the wall, yet has excellent slip properties so patterns can easily be matched. In premixed pastes, METHOCEL is used to control viscosity and improve wet tack. Pastes made with METHOCEL cellulose ethers are easily cleaned up with water and don't provide a source of nourishment for insects.

Latex adhesives. METHOCEL products are used as thickeners in a variety of latex adhesives, such as adhesives used in shoe manufacturing. Fast drying speeds and high wet-tack strength due to thermal gelation are key benefits in many of these applications.

Agricultural Chemicals

Dispersing agents. METHOCEL cellulose ethers are used as suspending and dispersing aids for wettable pesticide and fertilizer powders. They provide high wet tack and adhesion to waxy plant surfaces. Chemically inert and nonionic, METHOCEL cellulose ether is compatible with a wide range of active ingredients.

Spray adherents. Spray adherents or "seed stickers" made with METHOCEL products effectively bind pesticides, inoculants, and nutrients to seeds. METHOCEL products feature low plant toxicity and won't harm germinating plants.

Ceramics Processing

Tape casting. Use of METHOCEL products provides better flow and leveling and more uniform thickness. Low sodium residues provide the purity necessary for electronic items. Thermal gelation reduces binder migration and surface faults.

Extrusion forming. Used as a temporary binder and processing aid, METHOCEL cellulose ethers allow precise control of rheology in ceramic mixes, permitting broader operating ranges. Lubricity reduces energy consumption and die wear, and promotes smoother surfaces. Thermal gelation permits extrusion of extremely delicate, thin-walled shapes without sag or deformation.

Dry and isostatic pressing.

METHOCEL products provide optimum grain lubrication for tighter, more uniform packing. The results are more predictable green densities, less shrinkage during firing, and higher fired strengths.

Glazes/porcelain enamel.

METHOCEL cellulose ethers improve control of viscosity and rheology and fire out completely in the kiln.

Injection molding. Use of METHOCEL cellulose ethers provides higher green densities and better green strength. In high-temperature coatings/refractory mixes and mortars, METHOCEL improves workability and application properties. Because METHOCEL products have low ionic salt residues, they won't lower melting points. In fact, they can permit a reduction in use of plasticizers with low melting points.

Chemical Specialties

Resins. METHOCEL cellulose ethers are used to control rheology and as a colloidal stabilizer in a variety of epoxy, fiberglass, and urea-formaldehyde resins.

METHOCEL provides ideal flow and leveling characteristics, plus quick-set properties due to thermal gelation.

Rubber. METHOCEL products are used as mold-release agents, stabilizers, and thickeners in rubber latexes. METHOCEL cellulose ethers contribute to more uniform drying and less pinholing.

PVC suspension polymerization.

METHOCEL products are used in PVC polymerization as primary and secondary suspension agents. They provide excellent particle size control, good porosity for improved plasticizer absorption, low reactor scaling, and high bulk densities.

Construction Products

Drywall tape-joint compounds.

METHOCEL products impart workability, shrink and crack resistance, slip, and adhesion in tape-joint compounds. Water retention properties increase open times and help maintain a wet edge.

Cement-based tile mortars.

METHOCEL cellulose ethers provide water retention and workability to Portland cement-based ceramic tile mortars and grouts. They also improve adhesion, reduce skinning, and increase open time.

Masonry mortars. Used as performance additives in masonry mortars, METHOCEL products extend board life and improve workability. METHOCEL also contributes to air entrainment, often reducing the need for other additives for this purpose.

Gypsum adhesives and gypsum and cement hand and spray plasters.

METHOCEL cellulose ethers impart workability, pumpability, and consistency to adhesives and hand and spray plasters. They also provide water retention and antisag properties.

Wall and ceiling textures.

METHOCEL products impart pumpability, adhesion, workability, and water retention in wall and ceiling texturizing products.

Cement plaster and stucco.

METHOCEL cellulose ethers provide water retention for proper curing, improved workability, and pumpability.

Foods

Bakery products. Thermal gelation aids in gas retention during baking, increasing baked volumes and improving texture. METHOCEL also provides a more moist texture, increased shelf life, improved emulsification of batters, and better freeze/thaw stability.

Confections. In glazes, icings, and coatings, METHOCEL food gums add lubricity for easier application, provide creamier texture, improved spreadability, and clean flavor release. In addition, METHOCEL gums thermally gel during heating, keeping icings and glazes intact, and during cooling revert to the original consistency of the product.

Pie and pastry fillings. Thermal gelation reduces boil-over during baking and inhibits moisture migration from fillings to crusts during freezing. METHOCEL also improves freeze/thaw stability.

Frozen desserts. METHOCEL products modify ice-crystal size to give smoother textures and improve emulsion stability. Increased air entrainment improves overrun.

Whipped toppings. METHOCEL products improve whipping properties for better body and appearance. Improved emulsion stability prevents syneresis and extends open times. METHOCEL inhibits phase separation in frozen toppings, even through repeated freeze/thaw cycles.

Structured vegetable products.

METHOCEL products offer excellent film formation and high binding performance for foods that need to keep their components together. Products like vegetarian burgers, onion rings, and formed potato products are all improved by the binding strength and film formation qualities of METHOCEL products.

Structured and extruded foods. Low concentrations of METHOCEL give optimum binding strength in matrix systems. Due to moisture retention and oil insolubility properties, fried foods are more moist, less greasy. Thermal gelation gives increased control over texture and "bite." Increased lubricity aids in processing.

Frying batters. In addition to forming an oil-insoluble barrier to block oil absorption and moisture loss during frying, METHOCEL products improve adhesion of batters to meat and vegetable substrates. As a result, blow-off of batters is reduced and the life of frying oil is extended.

Salad dressings and sauces. Better stability for oil-in-water emulsions extends the shelf life of products containing METHOCEL. Solids stay in suspension longer and body and pouring characteristics are controlled.

Gelled Fuels

Fuel thickeners. METHOCEL cellulose ethers are used as thickeners for gelled alcohol used in charcoal lighters, restaurant candles, and canned-fuel products.

Household Products

Cleaners and detergents. Use of METHOCEL provides viscosity control, cling, foaming, soil anti-redeposition, and emulsion stabilization to household cleaners and detergents.

Paints

Latex paints. METHOCEL cellulose ethers are used as thickeners, protective colloids, and pigment-suspension aids in latex paints. They provide high enzyme resistance which helps stabilize viscosity. Film-forming properties contribute to better paint film quality with fewer pinholes. The product uniformity offered by METHOCEL cellulose ethers can mean lower quality control costs and more predictable performance for paints. Their use also improves wet-edge retention. They offer flexibility and ease of incorporation.

Paint Removers

Scrape-off and flush-off paint removers. The unique combination of organic and water solubility offered by METHOCEL products makes them ideal thickeners for scrape-off and flush-off paint removers (both methylene chloride and alternative paint strippers). They provide the thickening and cling needed to retain the paint remover on vertical or inclined surfaces, yet permit the softened paint to be rinsed off easily with water.

Paper Products

Grease-proof coatings, adhesives, release coatings, and surface sizings. Grease and oil barrier properties, in conjunction with film-forming capabilities, make METHOCEL valuable in a variety of paper coatings and sizings. The excellent film properties (high tensile strength and good elongation) offered by METHOCEL play key roles in these applications.

Personal Care Products

Shampoos. METHOCEL cellulose ether is widely used as a thickener in shampoos. Because the thickening performance of METHOCEL doesn't depend on a high surfactant

level, it's the thickener of choice for shampoos designed for dry and normal hair. METHOCEL also helps stabilize foams, so shampoos have better lather characteristics.

Body Gels. The natural lubricity of METHOCEL products can improve product flow, aid in dispensing and enhance sensory characteristics. Just as in shampoos, METHOCEL cellulose ethers add texture and provide a superior volume of lubricious, stable lather especially important in the formation of bubble baths and shower gels.

Creams and lotions. METHOCEL can contribute film-forming and secondary-thickening properties which improve after-feel and other sensory characteristics in creams and lotions.

Pharmaceuticals

Tablet coatings. METHOCEL cellulose ethers form strong films with good adhesion. They provide taste-masking films and act as excellent barriers for water-sensitive drugs or components. Coatings of METHOCEL also increase compressive strength and reduce friability.

Granulation. Used at low concentrations as binders in the granulation process, METHOCEL products produce hard tablets with low friability, yet don't negatively affect tablet disintegration. METHOCEL allows the reduction of compression force, an important factor in extending the life of tooling and equipment.

Controlled release. METHOCEL cellulose ether can be used for controlled-release pharmaceuticals using two different methods. It is used in hydrophilic-matrix tablets or capsules as described in a separate bulletin on sustained release. In addition, METHOCEL is used in diffusion control films comprised of METHOCEL cellulose ethers and

ETHOCEL* ethylcellulose resins. The water-soluble METHOCEL dissolves out of the film, leaving the water-insoluble ETHOCEL ethylcellulose. Drug diffusion and film porosity are controlled by the amount of METHOCEL used.

Water-soluble thermoplastics.

METHOCEL cellulose ethers can be heated and mixed with a plasticizer for extrusion or molding into a wide range of physical forms. This process is used to produce single-unit matrix tablets; multiparticle delivery, such as extruded beads or chips; transdermal patches; suppositories; or liquid-filled hard-shell capsules.

Liquid preparations. METHOCEL products are used in oral and topical liquid pharmaceuticals because they are excellent thickeners, improve emulsion stability, suspend solids, lubricate, and retain moisture. The protective colloid action and emulsifying properties of METHOCEL also benefit many liquid formulations.

Printing

Printing inks. METHOCEL cellulose ethers are used as thickeners and suspending agents for water-based inks.

Textiles

Textile printing pastes. Used as emulsion stabilizers in textile printing pastes, METHOCEL cellulose ethers help keep inks from wicking into fabrics.

Fabric sizings. METHOCEL helps hold fibers together, which strengthens fabrics during manufacturing processes. The lubricity of METHOCEL helps cut friction, permitting faster equipment speeds.

Temporary adhesives. Excellent wet-tack and quick-set properties make METHOCEL an ideal temporary fabric adhesive.

Regulated Uses

Chemical Inventory

METHOCEL products, methylcellulose and hydroxypropyl methylcellulose, comply with all applicable rules and orders under Toxic Substances Control Act PL94-469. The Chemical Abstracts Services Registry No. (CAS) is 9004-67-5 for methylcellulose and 9904-65-3 for hydroxypropyl methylcellulose.

METHOCEL products have also been reported for the following inventories:

European Inventory of Existing Chemical Substances (EINECS)

Australia Inventory of Chemical Substances (AICS)

Ministry of International Trade and Industry Inventory (MITI, the Japanese inventory)

Canadian Domestics Substances List (DSL)

Many countries are in the midst of creating new chemical inventories.

Pharmaceuticals

Premium grades of METHOCEL A, METHOCEL E, METHOCEL F, and METHOCEL K products are used for pharmaceutical and topical applications. Premium grades of METHOCEL products meet the specifications of the United States Pharmacopoeia (USP XXIII), European Pharmacopoeia (EP) and Japanese Pharmacopoeia (JP) and are listed as methylcellulose and hypromellose¹. In addition, methylcellulose (METHOCEL A products) is Generally Recognized As Safe (GRAS) by the U.S. Food and Drug Administration.

To support new drug applications in the United States, masters files for these products are on file at the Bureau of Drugs of the U.S. Food and Drug Administration.

Foods

METHOCEL food gums have long been used in the food industry. METHOCEL food gums are approved within the Food Chemicals Codex and are listed as methylcellulose and hydroxypropyl methylcellulose.

In the U.S., methylcellulose is approved as a multiple purpose GRAS food substance according to 21CFR 182.1480. It is also allowed for use in meat products according to 9CFR 318.7 and 9CFR 381.147. Hydroxypropyl methylcellulose is approved for direct food use by the FDA under 21CFR 172.874. It is also approved by the USDA as an emulsifying agent, binder, thickener, and stabilizer and is listed in the Standards and Labeling Policy Book published by the USDA. Because they are approved for direct food use, METHOCEL products can also be used as packaging components and in indirect food applications.

In the European Union, METHOCEL food gums are approved for use within the European Directive 95/2/EC. Hydroxypropyl methylcellulose and methylcellulose are included in Annex I of this Directive.

When labeling these food ingredients, one can use either their proper chemical names or their common names. Therefore, one could use "methylcellulose" or "modified vegetable gum" for METHOCEL A products. For

METHOCEL E, F, or K products, one could use "hydroxypropyl methylcellulose" or "carbohydrate gum." METHOCEL products are also certified as kosher for yearround and Passover use by the Union of Orthodox Jewish Congregations of America.

Pesticide Use

Under 40CFR 180.1001, certain inert ingredients used in pesticide formulations are exempt from the requirements of a tolerance. Methylcellulose and hydroxypropyl methylcellulose may be used in formulations applied to growing crops or raw agricultural commodities after harvest. Both Standard and Premium grade METHOCEL cellulose ether products are appropriate.

¹ The former official monograph name of hypromellose was "hydroxypropyl methylcellulose" or "HPMC."

How To Prepare Aqueous Solutions of METHOCEL Cellulose Ethers

METHOCEL cellulose ether products are carbohydrate polymers which dissolve in cold water (and in some instances in certain organic solvents) by swelling and subsequent hydration. There is no sharp solubility limit such as occurs in the dissolution of ionizing salts. The concentration of METHOCEL in solution is usually limited by the viscosity that a manufacturer is equipped to handle. It also depends on the viscosity and chemical type of METHOCEL product used. Solutions of lowviscosity products can be made at 10% to 15% concentration. Highviscosity products find a normal limit at 2% to 3% concentration.

The form of METHOCEL cellulose ether product chosen (powder or surface-treated powder, or granules) influences the techniques used to make solutions. Surfacetreated and granular products can be added directly to aqueous systems. They disperse readily with mild agitation and dissolve (build viscosity) gradually under neutral conditions. The dissolution rate of surface-treated products can be increased by adjusting to an alkaline pH after dispersing the powder in water. Although untreated METHOCEL powders are soluble in cold water, they must first be thoroughly dispersed in the water to prevent lumping.

Working with Surface-treated Dispersible Powders

In many applications, the combination of easy dispersion in cold water and rapid hydration (viscosity build) is desirable. Surface-treated METHOCEL powders are chemically treated so that they become temporarily insoluble in cold water. This allows

the METHOCEL product to be added to a formulation and dispersed at relatively low shear without any significant viscosity increase initially.

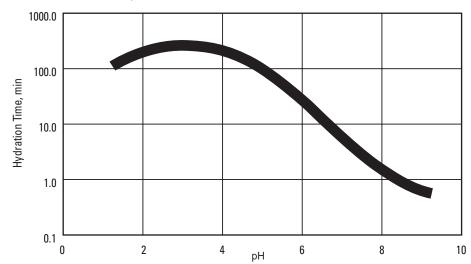
The "time delay" of the hydration or viscosity build is a function of the level of surface treatment as well as temperature, pH of the system, and concentration of the METHOCEL product. Normally, the concentration of METHOCEL in the system does not become a factor until the concentration exceeds 5% by weight (relative to water in the system). At higher concentrations, the time of hydration (referred to as delay time) is reduced. The delay time is generally reduced as temperature is raised. Figure 2 shows a typical delay time as a function of pH, evaluated at room temperature.

In many cases it is desirable to "trigger" viscosity build immediately following dispersion. Aqueous slurries can be held for 45 minutes and still remain usable in neutral

systems. A trigger can conveniently be used by adding a small amount of a base, such as ammonium hydroxide, sodium bicarbonate, etc. If METHOCEL is dispersed in neutral water (pH approximately 7), there is adequate time for thorough dispersion. Addition of base to raise the pH to approximately 9 causes the hydration to be completed in just a few minutes.

For best results and to achieve maximum hydration, surface-treated powders should be added with good agitation to a neutral pH system. The system should be agitated thoroughly for a few minutes, followed by an adjustment of pH to 8.5 to 9.0 with continued agitation, until full viscosity is reached (usually 10 to 30 minutes). Once the pH has been shifted to the alkaline side (pH 8.5 to 9.0), allowing full and rapid solubilization of the surface-treated product, solutions are stable over the pH range of 3 to 11.



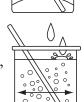


The addition of a slurry to an alkaline pigment grind or filler dispersion, or the addition of a slurry to a basic pigment-latex formulation, provides rapid solubilization and uniform viscosity development. The addition of dry, alkaline pigments or fillers to a slurry on high-speed or low-speed mixing equipment also results in rapid solubilization and viscosity development.

CAUTION: Attempts to adjust the pH of high-concentration slurries may lead to excessively high viscosity so that they cannot be pumped or poured. The pH adjustment should be made only after a slurry is diluted to the concentration at which it will be used.

Dispersion Technique

1. Add the surfacetreated METHOCEL powder to the water. Begin agitation.



2. Continue agitation and add sufficient ammonium hydroxide, sodium bicarbonate, or other alkaline material (e.g., pigment grind) to the dispersion to obtain a pH of 8.5 to 9.0. This will result in rapid viscosity development. Continue agitation

until sufficient hydration has

been achieved.

Working with Untreated Powders

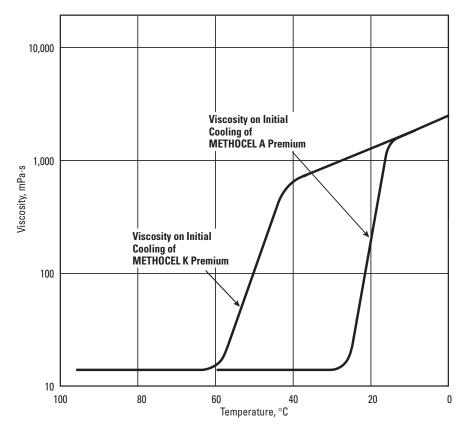
Although METHOCEL powders are soluble in cold water, they must first be thoroughly dispersed in the water to prevent lumping. In some applications, dispersion can be accomplished at ambient temperatures or in cold water by using an eductor funnel or highshear mixer. However, if untreated powders are added directly to cold water without sufficient agitation, a lumpy solution may result. Lumping results from incomplete wetting of the individual powder particles. Only part of the powder dissolves, a gelatinous membrane which shields the remaining powder from complete hydration. Several dispersion techniques are commonly used and are described below. Each has advantages in certain applications.

Dispersion in Hot Water

Often called the "hot/cold" technique, this method takes advantage of the insolubility of METHOCEL cellulose ethers in hot water. The powder is first dispersed by mixing thoroughly with 1/5 to 1/3 of the total required volume of water that has been heated to above 90°C (194°F). Mixing continues until all particles are thoroughly wetted.

For complete solubilization, the remainder of the water is then added as cold water or ice to lower the temperature of the dispersion. Once the dispersion reaches the temperature at which that particular METHOCEL product becomes water soluble, the powder begins to hydrate and viscosity increases.

Figure 3: Viscosity Development of METHOCEL A and METHOCEL K Products Slurried at 2% in Hot Water



In some applications, it may be desirable to heat the entire volume of water, disperse the METHOCEL powder, then cool the mixture while agitating until hydration is complete. It is very important, however, to have adequate cooling after wetting with hot water to ensure complete hydration and viscosity development.

For improved clarity and reproducible control of viscosity, solutions of METHOCEL A cellulose ether products (methylcellulose) should be cooled to 0° to 5°C (32° to 41°F) for 20 to 40 minutes. In general, solutions of METHOCEL E, METHOCEL F, METHOCEL J, and METHOCEL K brand cellulose ethers (hydroxypropyl methylcellulose) require cooling to 20° to 25°C (68° to 77°F) or below.

Because complete hydration depends on adequate cooling, METHOCEL E, F, J, and K brand products are frequently used in applications where cold water is not available. Figure 3 illustrates the effects of cooling hot slurries of METHOCEL A and METHOCEL K products. This figure shows that a slurry of METHOCEL K brand cellulose ether requires much less cooling for hydration than a slurry of METHOCEL A cellulose ether. Slurries of METHOCEL E, F, and J brand products also require less cooling than METHOCEL A brand products.

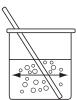
Dispersion Technique

1. Heat approximately 1/3 the required volume of water to at least 194°F (90°C).





- 2. Add the METHOCEL powder to the heated water with agitation.
- 3. Agitate the mixture until the particles are thoroughly wetted and evenly dispersed.



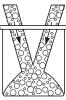


- 4. For complete solubilization, add the remainder of the water as cold water or ice to lower the
- temperature of the dispersion. Once the dispersion reaches the temperature at which that particular METHOCEL product becomes water soluble, the powder begins to hydrate and viscosity increases. See pages 12 and 13 for cooling times and temperatures for specific METHOCEL products.
- 5. Continue agitation for at least 30 minutes after the proper temperature is reached. Your solution of METHOCEL cellulose ether is now ready to use.

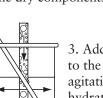
Dispersion by Dry-Blending

Dry-blending involves mixing METHOCEL powder with other dry ingredients before adding the water component. Dry-blending separates the particles of METHOCEL cellulose ethers to allow thorough wet-out and complete hydration when water is added. The minimum ratio of other dry, powdered ingredients to METHOCEL powder varies from 7:1 to 3:1.

Dispersion Technique



- 1. Combine METHOCEL powder with other dry-powder ingredients. The suggested ratio of other dry-powder ingredients
- to METHOCEL is 7:1; however, the ratio may vary from 7:1 to 3:1.
- 2. Thoroughly blend the dry components.



- 3. Add the dry mix to the water with agitation. The rate of hydration will depend upon both the relative
- particle sizes and the rate of agitation during and after addition of the mixture to the water.
- 4. Agitate until the METHOCEL powder has completely hydrated and the solution is consistently smooth. Your solution of METHOCEL cellulose ether is now ready for further processing.

Dispersion in Concentrated Salt Solutions

Both untreated and surface-treated METHOCEL cellulose ethers can be dispersed in concentrated salt solutions. Dissolution occurs when the brine is diluted with cold water.

How To Prepare Solutions of METHOCEL Cellulose Ethers in Nonaqueous Solvents and Nonsolvent Media

Solubility in Nonaqueous Solvents

The solubility of METHOCEL cellulose ethers in nonaqueous media varies according to the nature and quantity of substituent groups on the anhydroglucose chain. When using a water-miscible, organic solvent, such as an alcohol or glycol, use a ratio of at least 5 to 8 parts of solvent to 1 part METHOCEL.

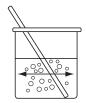
Dispersion in Non-solvent Media

Untreated METHOCEL cellulose ethers may also be dispersed in non-solvent media such as vegetable oil, propylene glycol, polyethylene glycol, glycerine, corn syrup, and high-fructose corn syrup. A ratio of 5 to 8 parts non-solvent to 1 part METHOCEL is recommended to obtain a fluid slurry. The dispersion of METHOCEL in a non-solvent medium may then be added to cold water, or the cold water may be added to the dispersion.

Dispersion Technique

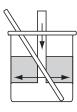


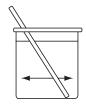
1. Add the METHOCEL cellulose ether to the non-solvent. A ratio of 5–8 parts non-solvent to 1 part METHOCEL is recommended to obtain a liquid slurry.



2. Agitate the mixture and METHOCEL powder until the particles of METHOCEL cellulose ether are evenly dispersed.

3. The dispersion of METHOCEL in a non-solvent medium may be added to cold water, or the cold water may be added to the dispersion.





4. Continue mixing until the METHOCEL powder is completely hydrated and the solution is smooth. You can now add the remaining ingredients in your formulation.

Properties of METHOCEL Cellulose Ethers in Powder Form

METHOCEL cellulose ether products are white to slightly off-white powders which are essentially odorless and tasteless. The apparent density of the powders ranges from 0.25 to 0.70 g/cm³ (250–700 kg/m³).

Moisture Sorption

METHOCEL products sealed in their original shipping containers absorb little to no atmospheric moisture. Once a container is opened, however, there is pickup of moisture from the air. When "exposed" METHOCEL cellulose ether is weighed, a portion of the total weight, therefore, may be water. Such weight must be corrected for moisture content to ensure that the proper weight of METHOCEL is used to give the desired viscosity.

To minimize moisture pickup, opened bags should be tightly resealed. The moisture-sorption rate of METHOCEL K brand products is somewhat greater than for METHOCEL A brand products. However, the moisture-sorption rates are about the same within a single chemical type. Typical moisture sorption is shown in Figure 4.

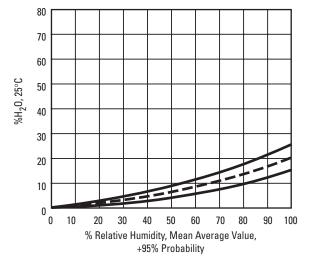
Resistance to Microorganisms

An important property of METHOCEL cellulose ether products is their high resistance to attack by microorganisms. METHOCEL products with higher degrees of substitution are especially resistant to enzymes. The fact that virtually all METHOCEL methylcellulose and METHOCEL hydroxypropyl methylcellulose ethers pass through the intestinal tract essentially unchanged attests to the stability of these products to a wide range of biochemical and enzymatic systems. Shelf-life in paints and other latex-based coatings, and stability of solutions and other products containing METHOCEL cellulose ether, can be greatly increased by this resistance to microorganisms.

As the cellulose is modified by substitution with various radicals, such as alkyl and hydroxyalkyl groups, resistance to microbial attack increases. Several researchers have reported that the degree of substitution (D.S.) of water-soluble cellulose derivatives was a primary factor, with a threshold D.S. value of 1.0 required for protection.[†]

Because METHOCEL cellulose ether products have excellent uniformity of substitution, with a D.S. much higher than 1.0, they possess excellent resistance to microbial attack.

Figure 4: Equilibrium Moisture Content vs. Percent Relative Humidity, 25°C



[†]H.S. Levinson and E.T. Reese, *J. Gen. Physiol.* 33, No. 601 (1950). E.T. Reese, R.G.H. Siu, and H.G. Levinson, *J. Bacteriology* 59, No. 485 (1950). E.T. Reese, *Ind. Eng. Chem.* 49, No. 104 (1957).

Properties of Solutions of METHOCEL Cellulose Ethers

Some of the general solution properties of METHOCEL cellulose ether products are listed in Table 6.

Rheology of Solutions of METHOCEL Cellulose Ether

The rheology of solutions of METHOCEL plays an important role in many practical applications where the modification of flow behavior is essential (for example, paints, cosmetics, food products, building products). A Newtonian fluid is one whose viscosity is independent of shear rate (or velocity gradient of flow). In actual practice many systems exhibit non-Newtonian flow behavior where apparent viscosity may decrease (pseudoplastic) or increase (dilatant) with increasing rate of shear.

Rheology of an aqueous solution of METHOCEL is affected by its molecular weight, concentration, temperature, and by the presence of other solutes. In general, aqueous solutions of METHOCEL exhibit pseudoplastic flow behavior. Pseudoplasticity increases with increasing molecular weight or concentration. However, at very low shear rates, all solutions of METHOCEL cellulose ether appear to be Newtonian and the shear rate below which the solution becomes Newtonian increases with decreasing molecular weight or concentration. Figures 5 and 6 illustrate this behavior (the numbers on curves indicate viscosity types).

Table 6: General Solution Properties

Specific gravity, 4°C, all types 1% solutions 1.0012 5% solutions 1.0117 10% solutions 1.0245
Refractive index, 2% solutions, all types 1.336
Partial specific volume 4,000 mPa·s METHOCEL A 0.725 cm³/g (0.087 gal/lb) 4,000 mPa·s METHOCEL E 0.767 cm³/g (0.092 gal/lb) 4,000 mPa·s METHOCEL F 0.734 cm³/g (0.087 gal/lb) 5,000 mPa·s METHOCEL J 0.725 cm³/g (0.087 gal/lb) 4,000 mPa·s METHOCEL K 0.717 cm³/g (0.086 gal/lb) 15,000 mPa·s METHOCEL K 0.724 cm³/g (0.087 gal/lb)
Freezing point, 2% solutions, all types 0.0°C at 2% concentration
Surface tension, 25°C, 0.05% concentrationWater.72-74 x 10³ Newton/meter (72-74 dynes/cm)Methylcellulose.53-59 x 10³ Newton/meter (53-59 dynes/cm)Hydroxypropyl methylcellulose.43-55 x 10³ Newton/meter (43-55 dynes/cm)

Figure 5: Apparent Viscosity vs. Shear Rate, 2% Aqueous Solutions, 20°C

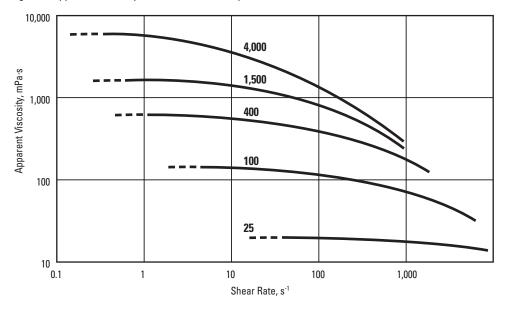
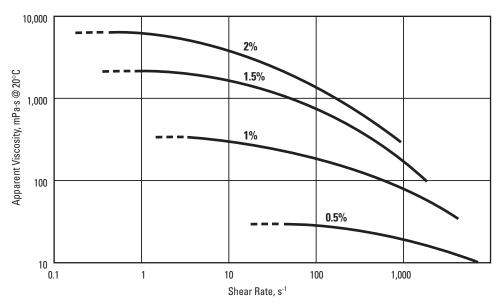


Figure 6: Apparent Viscosity vs. Shear Rate, for Aqueous Solutions of 4,000 mPa·s METHOCEL Cellulose Ethers at Various Concentrations



Molecular Weight/Viscosity Relationships

The apparent viscosity of an aqueous solution of a METHOCEL cellulose ether is proportional to the molecular weight or chain length of the specific METHOCEL product used. Commercial designations of METHOCEL products are based on viscosity values determined in water at 20°C, with a concentration of 2% METHOCEL. The measurement methods used are described in the current ASTM monographs D1347 and D2363. The correlation between the number average molecular weight (Mn) and the commercial viscosity designation for METHOCEL A cellulose ethers is shown in Figure 7.

Table 7 provides further information regarding the correlation of number average molecular weight with the commercial viscosity designation. Intrinsic viscosity is the limiting quotient of the specific viscosity divided by the concentration as infinite dilution is approached (as the concentration approaches zero). The number average molecular weight (Mn) is calculated from the limiting osmotic pressure of the solvent as the concentration of the solute approaches zero. The average molecular weight (Mw) will be 3 to 10 times the Mn.

Effect of Concentration on Viscosity

Most formulations require a predetermined product viscosity of METHOCEL cellulose ether. Figure 8 shows how the concentration of METHOCEL products of varying viscosity affects the aqueous solution viscosity at 20°C. The measurements were made using an Ubbelohde viscometer (ASTM D2363). Data for both low and high molecular weight METHOCEL products are shown and represent the average material found within a viscosity specification.

Figure 7: Molecular Weight/Viscosity Correlation, 20°C

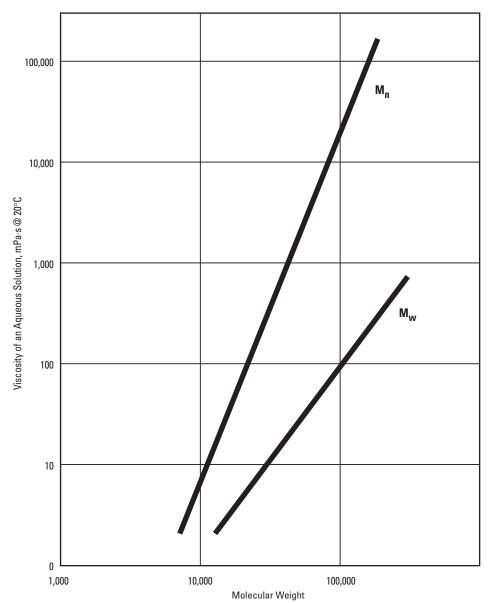


Table 7: Viscosity of Methylcellulose of Various Molecular Weights

Viscosity Grade 2%, 20°C, mPa·s	Intrinsic Viscosity (h), dL/g	Number Average Degree of Polymerization	Number Average Molecular Weight (Mn)
5	1.2	53	10,000
10	1.4	70	13,000
40	2.0	110	20,000
100	2.6	140	26,000
400	3.9	220	41,000
1,500	5.7	340	63,000
4,000	7.5	460	86,000
8,000	9.3	580	110,000
15,000	11.0	650	120,000
19,000	12.0	750	140,000
40,000	15.0	950	180,000
75,000	18.4	1,160	220,000

This graph is plotted on an 8th root scale, not a logarithmic scale. The 8th root of the viscosity is a roughly linear function of the concentration.

The equation which expresses the illustrated approximate relationship between solution viscosity and polymer concentration is $\eta^{1/8} = (C \cdot \alpha) + 1$, where η is the solution viscosity in millipascal-seconds, C is the polymer concentration in solution (expressed in percent), and α is a constant specific to the molecular weight. The value of α may be calculated by substitution and may then be used to calculate the approximate viscosity at the desired concentration.

For example, for a 4,000 mPa·s product, $(4,000)^{1/8} = (C \cdot \alpha) + 1$. Solving for α yields a value of 0.910. For a 1,500 mPa·s product, $(1,500)^{1/8} = (C \cdot \alpha) + 1$. Solving for α yields a value of 0.747. Having calculated α for a particular METHOCEL product, this value can be used to calculate viscosity at other concentrations.

To find the line for any intermediate grade, locate the desired 2% viscosity above 2% on the abscissa and draw a straight line to the point of origin.

Blending for Intermediate Viscosity

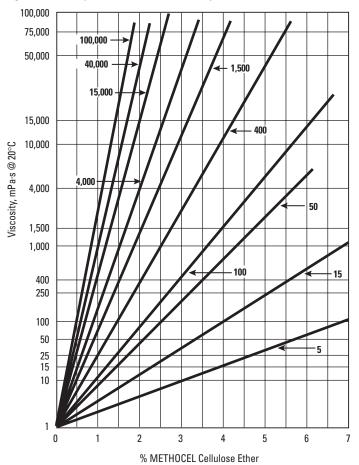
METHOCEL products of the same substitution type, but of different viscosity grades, can be blended to obtain an intermediate viscosity grade. Figure 9 is a blending chart that can be used for this purpose.

To use the chart, mark the viscosity of one material along the left axis (Scale A) and the viscosity of the other material along the right axis (Scale B). Connect the two points in a straight line that crosses the graph. In the example shown, the viscosities of the

starting materials are 400 mPa·s on the left and 15,000 mPa·s on the right.

Now find the desired final viscosity on either axis and draw a horizontal line that intersects with the first line. From this intersection point, draw a vertical line down to the bottom scale. The number of that scale shows the percentage of Scale B Material needed in the blend. In this example 4,000 mPa·s is the desired final viscosity. So the required blend is 60% of the 15,000 mPa·s (Scale B) material and 40% of the 400 mPa·s (Scale A) material.

Figure 8: Viscosity/Concentration Relationships



The relationship may be expressed mathematically as: $\eta_B^{1/8} = x_1 \eta_1^{1/8} + x_2 \eta_2^{1/8}$, where x_1 and x_2 are the weight fractions of components one and two, respectively.

The example on the chart shows that 60% of 15,000 mPa·s material and 40% of the 400 mPa·s material are needed to make a blend having a viscosity of 4,000 mPa·s.

Effect of pH on Viscosity

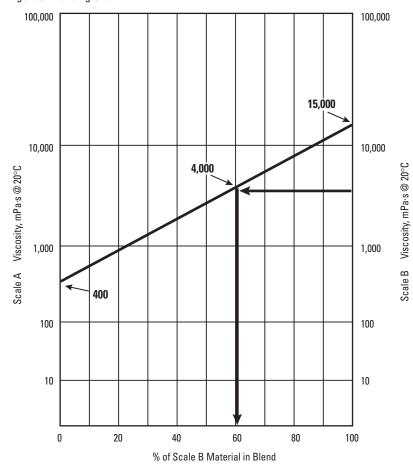
Because METHOCEL products are nonionic, the viscosities of their solutions are generally stable over a wider pH range than are the viscosities of gums that are ionic in nature. Outside the range of pH 3 to 11, however, there may be a gradual loss of viscosity at higher temperatures or after long periods of standing, especially with high-viscosity solutions. Solutions of METHOCEL cellulose ethers in acids or in strong caustic solutions will decrease in viscosity. This factor should be considered when determining the shelf life of products.

Effect of Additives on Viscosity

In the preparation of formulations, viscosities may occasionally result which are considerably higher than expected. This phenomenon can be caused by the interaction of METHOCEL with one or more of the formula ingredients. As a result, it may be possible to use less thickener and still have adequate viscosity.

This effect usually passes through a maximum that is dependent on the concentration of the interacting materials and on the presence of other ingredients such as pigments, latex particles, or preservatives.

Figure 9: Blending Chart



In systems having lower concentrations of additives (~1%), METHOCEL A or METHOCEL F products are frequently suitable. In systems where the concentration of additives is rather high (~10%), the more highly substituted products such as METHOCEL E, J, or K products may be more compatible.

Effect of Freezing on Solutions

Solutions of METHOCEL cellulose ether products do not undergo separation into phases upon freezing. There is no separation of fluid layers (syneresis) or formation of insoluble precipitates or haze. This lack of phase separation on freezing is particularly important in frozen food items. As solutions of METHOCEL cellulose ether products are cooled, solubilization increases, as evidenced by increasing viscosity and improved clarity of solutions. When the solutions freeze, part of the water is held in the latent super-cooled state and does not freeze. The heat normally released on freezing (heat of fusion) is decreased by the amount of the super cooling.

Defoamers for Aqueous Solutions

The foaming of solutions of METHOCEL cellulose ethers is easily controlled by using foam stabilizers and defoamers.

Defoamer concentrations should be kept to the minimum required because these materials are generally low in water solubility. The choice of a defoamer depends on the type of surfactant, latex, and other ingredients in the system. For defoaming complex systems, consultation with the supplier of defoamers is suggested.

Antifoam agents are extremely efficient surface-active compositions which displace other surface-active substances at the air/water interface. Their use, therefore, might interfere with the performance of METHOCEL products in applications where the mechanical properties of solution-surface films is critical.

Preservatives for Aqueous Solutions

METHOCEL cellulose ethers normally do not require preservatives. They are not, however, antimicrobial agents. If contamination occurs, microorganism growth will not be inhibited.

To preserve solutions of METHOCEL, addition of 0.05% to 0.15% of DOWICIDE* A antimicrobial or DOWICIL* 75 preservative is suggested. More information on these products is available upon request. For regulated uses, you should use the appropriate permitted preservative.

Compatibility of Aqueous Solutions

The methylcellulose molecule is nonionic and is not precipitated as an insoluble salt by multivalent metal ions. However, METHOCEL cellulose ethers can be salted out of solution when the concentration of electrolytes or other dissolved materials exceeds certain limits. This is caused by competition of the electrolytes for water and results in reduced hydration of the cellulose ether.

Because of the difference in the amounts of organic substitution, METHOCEL E, F, J, K, and 310-Series brand hydroxypropyl methylcellulose products generally exhibit a higher tolerance for salts in solution than METHOCEL A brand methylcellulose products. There is only a slight variation in electrolyte tolerance among the various METHOCEL hydroxypropyl methylcellulose products.

Water-insoluble materials such as pigments, fillers, etc. will not adversely affect METHOCEL cellulose ethers. Actually, solutions of METHOCEL often serve as excellent dispersing media for such materials. Other water-soluble substances, such as starches, glues, and resins, may or may not be compatible with METHOCEL. Tests should be run on these materials to determine compatibility. Because METHOCEL cellulose ether products are not soluble in concentrated salt solutions. these media can be used as non-solvent dispersing media for non-surface-treated METHOCEL products. Subsequent dilution reduces the salt concentration to a level that allows dissolution of the METHOCEL product.

^{*} Trademark of The Dow Chemical Company

Thermal Gelation in Aqueous Media

METHOCEL cellulose ethers possess unique solubility properties in aqueous media. These products are insoluble in water that has been heated above a particular temperature. Below those temperatures, the solution and solubility of the METHOCEL cellulose ether products increase as the temperature is lowered. Aqueous solutions of METHOCEL cellulose ethers will gel when heated to temperatures that are specific for each type. The gels are completely reversible and the solutions liquefy upon cooling. This unique bulk thermal-gelation property proves valuable, compared to that of other natural and synthetic gums, in a wide variety of applications.

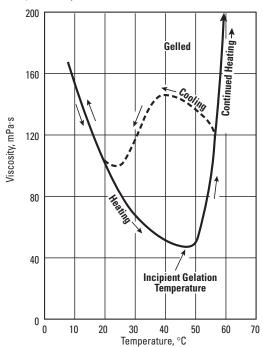
Bulk thermal gelation of aqueous solutions of METHOCEL is thought to be primarily caused by the hydrophobic interaction between molecules containing methoxyl groups. In a solution state at lower temperatures, molecules are hydrated and there is little polymer-to-polymer interaction other than simple entanglement. Figure 10 shows the viscosity of a typical solution as it is heated to its gel temperature, then cooled to the original temperature.

As the temperature of the solution is increased, the cellulosic polymers gradually lose their water of hydration, and viscosity decreases. When the gel point is reached, sufficient dehydration of the polymer occurs to cause a polymer-to-polymer association, and the solution begins to gel.

Gel strength continues to build as the temperature is held above the gel point.

When the solution is cooled, the gel effect begins to reverse and viscosity drops rapidly. Finally, the viscosity of the cooling solution merges with the original heating curve and increases as the temperature decreases. Once the solution has cooled, the viscosity is the same as it was originally. Thus, the thermal gelation process is reversible and can be repeated if desired.

Figure 10: Gelation of 2.0% Aqueous Solution of METHOCEL A100 Methylcellulose, Heating Rate 0.25°C/min



Controlling Gel Temperature

The specific temperature at which bulk thermal gelation occurs (the incipient gelation temperature or IGT) and the firmness of the gel are governed by the nature and quantity of the substituent groups attached to the anhydroglucose ring and, thus, vary with each type of cellulose ether. The molecular weight of the particular METHOCEL product selected has little effect on the gel temperature. However, increasing the concentration of the solution lowers the gel temperature as shown in Figure 11.

Within the range of viscosity available in the "A" type, the low-viscosity products will have gel points substantially higher than those of the high-viscosity products. The spread between high and low viscosity for the other METHOCEL cellulose ether types is relatively narrow.

The Effects of Heating Rate and Agitation on Gelation

Accurate measurement of gelation temperature requires care because it is a function of the rate of heating and the rate of shear. Both a high rate of shear and a fast heating rate result in an apparently high gel temperature.

Agitation also affects the strength of the gel. Continued rapid agitation during gelation may break down the gel structure and alter both the texture and strength of the gel. For maximum development of gel strength, heat the solution well above the gelation temperature under quiescent conditions.

Gel Strength and Texture

The texture and strength of gels produced by heating solutions of METHOCEL cellulose ethers varies with the product type, viscosity grade, and concentration of METHOCEL used. In applications where a strong, elastic gel is desired at slight elevations in temperature, METHOCEL A products are recommended. For softer, non-rubbery gels, METHOCEL F or E products should be used. For an even softer gel texture, METHOCEL K or METHOCEL J products are suggested.

In general, the strength of the gel increases sharply as molecular weight increases and gradually becomes constant at or above a viscosity of 400 mPa·s. Gel strength also increases with increasing concentration.

Effect of Concentration on Thermal Gelation

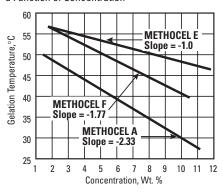
As the temperature of a solution of METHOCEL cellulose ether is raised, hazing of the solution occurs immediately prior to gelation, and the viscosity may start to rise. At this point, if the concentration is high enough, the solution will change to a soft or firm gel. If the concentration is below 0.5%, a fluid mixture of individual gel particles and water is formed, rather than a firm gel.

In general, as the concentration of METHOCEL cellulose ether is increased, the gelation temperature will be lowered. An increase of 2% in concentration can cause a 10°C drop in the gelation temperature for METHOCEL A cellulose ether products. A 2% increase in concentration of a solution of METHOCEL F cellulose ether product lowers the gelation temperature by only 4°C.

Interfacial Gelation

In addition to bulk-phase gelation, METHOCEL cellulose ethers also exhibit interfacial or surface gelation phenomena as a result of their surfactant nature. Interfacial gelation plays an important role in many

Figure 11: Gelation Temperature as a Function of Concentration



applications where a protective colloid, emulsification, or surfactant function is desirable. Examples include: suspension polymerization of vinyl chloride; aqueous foam stabilization in shampoos, bubble baths; and the stabilization of non-dairy whipped toppings and salad dressings.

To achieve bulk thermal gelation, concentrations of 1.5 wt % are generally necessary. However, even at concentrations as low as 0.001 wt %, many METHOCEL products exhibit surface thermal gelation due to the migration of polymer molecules to the air/water interface. Maximum gelation properties are achieved with METHOCEL A, E, and F.

The equilibrium concentration of METHOCEL products at any given interface depends upon the nature of the interface, presence of other solvents, temperature, and potential for formation of associative structures with other surfactants. However, the concentration of METHOCEL at an interface can be orders of magnitude greater than that presumed to be present in the bulk phase. As a result, surface film formation (surface gelation) occurs.

Table 8: Effect of Additives on Gelation Temperature for 2% Solutions of METHOCEL Cellulose Ether

Additive	% Additive	METHOCEL A15C, °C	METHOCEL F4M, °C	METHOCEL K4M, °C	METHOCEL J5M, °C
None	0	50	63	85	62
NaCl	5	33	41	59	42
MgCl ₂	5	42	52	67	50
FeCl ₃	3	42	53	76	53
Na ₂ SO ₄	5	salted out	salted out	salted out	salted out
Al ₂ (SO ₄) ₃	2,5	salted out	45	48	41
Na ₂ CO ₃	5	salted out	salted out	salted out	salted out
Na ₃ PO ₄	2	32	42	52	43
Sucrose ^a	5	51	66	84	60
Sucrose	20	44	59	61	53
Sorbitol	20	30	46	48	_
Glycerine	20	34	60	65-70	55
Ethanol ^a	20	>75	>75	>75	>78
Polyethylene					
Glycol 400°	20	52	>80	>80	>78
Propylene glycol ^a	20	59	>80	>80	>78

^aNote: This material raises the gelation temperature.

As a specific example, a 0.01 wt % solution of METHOCEL A15 LV cellulose ether exhibits surface gelation at 20°C, whereas bulk gelation with the same product would require a concentration exceeding 12 wt % at such a low temperature. A 0.01 wt % solution of METHOCEL A15 LV cannot be made to undergo bulk gelation at any temperature.

Surface gelation (filming) occurs very rapidly in many solutions of METHOCEL products whether dilute or concentrated. This effect is most evident (and troublesome) when one employs du Nouy tensiometry to determine surface tension.

Generally speaking, increasing the molecular weight, concentration, or temperature of a solution of METHOCEL will promote the onset of surface gelation just as in bulk thermal gelation.

Effect of Additives on Thermal Gelation

Additives may either increase or decrease thermal-gelation temperature, depending on whether the additive exhibits a coagulant or a solubilizing effect on the METHOCEL product. For example, solutes such as ethanol, PEG 400, and propylene glycol all raise the gel points of METHOCEL products.

This is due to the solubilizing effect which they impart. Additives such as glycerin, sorbitol, and salts lower gel points by lowering the solvency of the aqueous system, resulting in a more rapid dehydration of the METHOCEL product (Table 8).

If a manufacturer requires a high thermal gelation temperature and plans to use additives known to reduce the gel temperature, a METHOCEL product with a gel point higher than the temperature required should be used. As the concentration of the gel-causing additive increases, the thermal gel temperature decreases. Although the behavior of a particular solute must be determined empirically, the following general guidelines apply.

Additives Which Lower Gel Points

Most electrolytes, as well as sucrose, glycerine, etc., lower the gel point because they have a greater affinity for water and dehydrate the cellulosic polymer. Decreases in gel temperature are a function of the ions present in the additive.

Additives Which Raise Gel Points

The effect of an additive that raises gel point varies with different METHOCEL products. For example, the amount of propylene glycol required to increase the thermal gel point of a solution of METHOCEL A cellulose ether by 4°C will increase the gel point of a solution of METHOCEL F by 10°C and METHOCEL K by 20°C.

The increase in the thermal gel point is directly proportional to the increase in concentration of the additive. Figures 12 and 13 illustrate the relationship between concentrations of ethanol and propylene glycol and the thermal gel point of representative METHOCEL products.

Figure 12: Effect of Ethanol on Gel Temperature, 2% Solutions

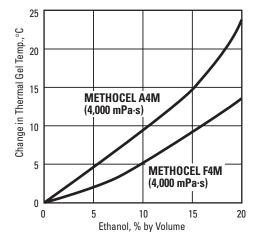
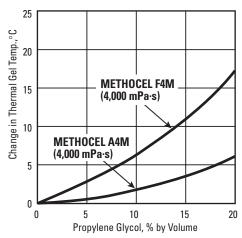


Figure 13: Effect of Propylene Glycol on Gel Temperature, 2% Solutions



Properties of Films of METHOCEL Cellulose Ethers

Table 9: Properties of Unplasticized Films of METHOCEL Cellulose Ethers

Properties ^a	METHOCEL A15 LV	METHOCEL E15 LV
Specific gravity	1.39	1.29
Area factor	24,000 in²/lb/mil	25,860 in²/lb/mil
Moisture vapor transmission rate, 100°F (38°C), 50% RH	67.5 g/100 in²/24 h/mil	65 g/100 in²/24 h/mil
Oxygen transmission rate, 75°F (24°C)	25 cm³/100 in²/24 h/mil	70 cm³/100 in²/24 h/mil
Tensile strength, 75°F (24°C), 50% RH	9,000 lb/in² (62 MPa)±10%	10,000 lb/in²(69 MPa) ±10%
Elongation, 75°F (24°C), 50% RH	5-15%	5-15%
Stability to ultraviolet light, 500 h, Fadeometer exposure	Excellent	Excellent
Resistance to oils and most solvents	Excellent	Excellent
Ultraviolet transmission (2 mil film) 400 nm 290 nm 210 nm	55% 49% 26%	82% 34% 6%

^aTypical properties, not to be construed as sales specifications. Data based on a 1 mil dry film.

High-strength, water-soluble films, supported or unsupported, may be rolled, cast, or extruded from formulations of METHOCEL cellulose ether products. These clear, smooth films or coatings are impervious to oils, greases, and most solvents. They are also effective binders, even when loaded with inert materials.

Tensile and elongation properties of typical films of METHOCEL cellulose ethers cast from water are shown in Table 9. The need for a plasticizer may be more pertinent when using low viscosity 5 mPa·s METHOCEL cellulose ethers because of lower film elongation properties. This can be more acute if drying temperatures are too high.

Effect of Additives on Film Solubility

The water solubility of films and coatings of METHOCEL cellulose ethers can be altered by the use of

cross-linking compounds and resins. The degree of insolubility can be controlled by the choice and quantity of a cross-linking reagent. All urea formaldehyde, melamine formaldehyde, and resorcinol formaldehyde resins can be used. Dialdehydes such as glyoxal are also effective. Supplier literature should be consulted for selection of catalysts and curing compounds.

Resistance of Films to Solvents

Films and coatings of METHOCEL are unaffected by animal and vegetable oils, greases, and petroleum hydrocarbons. Of the different types of products, METHOCEL A, METHOCEL F, and METHOCEL K brand products are most resistant.

Thermoplastic Forming

Procedures for preparing a dry-mix formulation of METHOCEL E or J cellulose ether products with propylene glycol and other plasticizers are available for extruded sheeting and injection or compression molding. Such mixes may be compounded in a ribbon-type blender at room temperature and satisfactorily handled by a feeder designed for powders. Most feeders perform better if the dry mix is first densified by being passed through a set of press rolls or through a pellet mill.

Flakes of METHOCEL E or J cellulose ether products with propylene glycol and other plasticizers may be extruded or molded directly into a finished, water-soluble product at temperatures ranging from 80 to 160°C (176 to 320°F). Properly plasticized sheet and tubing of METHOCEL cellulose ether can be heat-sealed at about 130°C (266°F).

Analytical Methods

Measuring Viscosity

Certain precautions must be observed for the accurate measurement of the viscosity of solutions of METHOCEL cellulose ethers because they exhibit a nonlinear shear stress/shear rate relationship, which results in pseudoplastic viscosity behavior at most shear rates.

Dow employs the ASTM reference method (D1347 and D2363) as its standard procedure. This method involves the use of Ubbelohde viscometers, one type for low viscosities and another for high viscosities. The Ubbelohde viscometer is a precision device which requires only a small test sample.

For measuring low viscosity, the appropriate capillary tube size is chosen to obtain a flow time of 50 to 150 seconds (see Table 10). The viscometer is placed in a 20°C bath, and the length of time required to deliver a given volume through the capillary tube is measured. The time in seconds is then converted to millipascalseconds (mPa·s). Detailed procedures are given in current ASTM standards D1347 and D2363. The most reproducible viscosities are obtained by cooling to 4°C and holding for at least one-half hour before testing at 20°C.

Viscosity may also be determined using a rotational viscometer such as the Brookfield model LVF[†] viscometer. When the viscosity of a solution is less than 500 mPa·s, the viscosity is less dependent on shear, and the solution may be regarded as near-Newtonian. The apparent viscosity of a solution of higher viscosity will be highly dependent on the rate of shear, decreasing as the rate of shear is increased.

The rotational instrument should be calibrated against standard oils. It's important to note, however, that there is no direct correlation between Ubbelohde and Brookfield measurements for non-Newtonian liquids. For details regarding analysis methods, please contact your local salesperson for METHOCEL cellulose ethers.

Table 10: Capillary Tubes for Measuring Viscosity

Viscosity, mPa·s	Size of Heavy Wall Tubing, Inside Diameter
Low viscosity	
15	1.5 mm
25	1.8 mm
100	2.4 mm
400	3.2 mm
High viscosity	
1,500	5.0 mm
4,000	6.0 mm
8,000	7.5 mm
15,000	10.0 mm
50,000	15.0 mm
75,000	15.0 mm
	I

Published Analytical Methods

Procedures for the analysis of METHOCEL cellulose ether products have been standardized under ASTM D1372 and ASTM D2372. These and other information on analysis are listed in the following references.

Methods for Testing Methylcellulose – Current ASTM D1372, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

Methods for Testing Hydroxypropyl Methylcellulose – Current ASTM D2372, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

Methoxyl and Hydroxypropyl Substitution in Cellulose Ether Products by Gas Chromatography – Current ASTM D3876, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

Methylcellulose – Food Chemicals Codex, Washington, D.C., National Academy of Sciences and National Research Council, Current Edition.

Hydroxypropyl Methylcellulose – Food Chemicals Codex, Washington, D.C., National Academy of Sciences and National Research Council, Current Edition.

The Determination of Particle Size Distribution of METHOCEL Cellulose Ethers – Dow Method No. Mc-l IA (1973).

Application of Anthrone Test to Determination of Cellulose Derivatives in Nonaqueous Media – Aldrich, J.C., Samsel, E.P., Anal. Chem. 29, 574-76 (1957).

Hydroxypropyl Methylcellulose – The National Formulary, American Pharmaceutical Association, Washington, D.C., Current Edition.

Colorimetric Determination of Methylcellulose with Diphenylamine – Danzaki, Grace, Berger, Eugene Y., Anal. Chem. 31, 1383-5 (1959).

Colorimetric Method for Determination of Sugars and Related Substances – Dubois, M., Gilles, K.A., Hamilton, J.K., Repers, P.A., Smith, F., Anal. Chem. 28, 350-356 (1956).

Methylcellulose – U.S. Pharmacopoeia, Bethesda, MD, The United States Pharmacopoeial Convention, Inc., Current Edition.

Determination of Alkoxyl Substitution in Cellulose Ethers by Zeisel-Gas Chromatography – Hodges, K., Kester, W., Wiederrich, D., Grover, J., Anal. Chem. 51, 2172-2176 (1979).

Handling Considerations

Material Safety Data Sheets/Safety Data Sheets for METHOCEL products are available from The Dow Chemical Company to help you further satisfy your own handling, disposal, and safety needs and those that may be required by government regulations. Such information should be requested prior to handling or use. The following comments are general and are not a substitute for the detailed safety information found in the Material Safety Data Sheet/Safety Data Sheet.

Health

METHOCEL cellulose ether products resemble the naturally occurring plant and seaweed gums in many of their chemical, physical, and functional properties. All of these materials possess a basic carbohydrate structure.

METHOCEL products have had extensive evaluation and testing in both acute and long-term feeding studies in a number of species, including humans. Their many years of use in a wide variety of food items attests to the safety of METHOCEL Premium products.

Although dust from METHOCEL cellulose ether products could conceivably cause temporary mechanical irritation to the skin and eyes under extreme conditions and may be considered a nuisance dust if inhaled, the products are considered to present no significant health hazard in handling. Please review the handling precautions within the Material Safety Data Sheet/Safety Data Sheet for more information.

Flammability

Cellulose ether products are organic polymers that will burn when exposed to heat and a sufficient oxygen supply. Fires can be extinguished by conventional

means, avoiding any raising of dust by strong water jets. Dow recommends the use of water spray, carbon dioxide, or powder extinguishers.

Storage

Caution: A fine dust of this material is capable of forming an explosive mixture with air. Powder samples should not be exposed to temperatures above 135° to 145°C. Samples may decompose and lead to a possible dust explosion. As in storage of any dusts or fine powders, good housekeeping is required to prevent dusts in air from reaching possibly explosive levels. When handling in large quantities or in bulk, the general precautions outlined in NFPA 63, "Prevention of Dust Explosions in Industrial Plants," and in NFPA bulletins 68, 69, and 654 are recommended.

With METHOCEL cellulose ether products with particle sizes of 74 µm or less (finer than 200 mesh), critical levels are reached at concentrations of 28 g/m³ (0.03 oz/ft³). The minimum ignition energy required to cause a dust explosion is 28mJ. Static from a human body has about 25mJ. This is normally not enough energy to ignite the powder.

As with any organic chemical material, METHOCEL cellulose ethers should not be stored next to peroxides or other oxidizing agents.

Accidental Spills and Housekeeping

Solutions of METHOCEL cellulose ethers are slippery. To prevent employee falls and injury, floor spills of dry powder should be thoroughly vacuumed or swept up. Any slight residual product on the walls or floor can then be flushed with water into a sewer. If the spill is a viscous solution, it should be further diluted

with cold water before disposal. Likewise, accumulation of dust should be avoided to control this hazard.

Disposal

Despite the very slow rate of biodegradation, cellulose ether products should not present any hazard in the waste/soil compartment. Their behavior is similar to wheat flour or sawdust. Although Dow studies using standard procedures showed no 5-day, 10-day, or 20-day BOD values, activated sludge studies with (14°) methylcellulose showed that methylcellulose was 96% degraded or otherwise removed from solution in 20 days. Thus, METHOCEL cellulose ethers should present no ecological hazard to aquatic life.

Because METHOCEL cellulose ether products and their aqueous solutions present no significant ecological problems, they can be disposed of by industrial incineration or in an approved landfill, providing regulations are observed. Incineration should be done under carefully controlled conditions to avoid the possibility of a dust explosion. Customers are advised to review their local, state, provincial or national regulations governing the disposal of waste materials to determine appropriate means of disposal in their area.

Customer Notice

Dow encourages its customers to review their applications of Dow products from the standpoint of human health and environmental quality. To help ensure that Dow products are not used in ways for which they are not intended or tested, Dow personnel will assist customers in dealing with ecological and product safety considerations. Please contact us at the numbers listed on the back cover.



toll-free +800 3 694 6367[†] call +32 3 450 2240 fax +32 3 450 2815

From Latin America and Other Global Areas:

call 1-989-832-1560 fax 1-989-832-1465

www.methocel.com

[†]Toll free from Austria (00), Belgium (00), Denmark (00), Finland (990), France (00), Germany (00), Hungary (00), Ireland (00), Italy (00), The Netherlands (00), Norway (00), Portugal (00), Spain (00), Sweden (00), Switzerland (00) and the United Kingdom (00).

NOTICE: No freedom from any patent owned by Seller or others is to be inferred. Because use conditions and applicable laws may differ from one location to another and may change with time, Customer is responsible for determining whether products and the information in this document are appropriate for Customer's use and for ensuring that Customer's workplace and disposal practices are in compliance with applicable laws and other governmental enactments. Seller assumes no obligation or liability for the information in this document. NO WARRANTIES ARE GIVEN; ALL IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE ARE EXPRESSLY EXCLUDED.

