METHOCEL Cellulose Ethers
Technical Handbook

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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. Table 1 provides an overview of these physical, chemical, and performance properties.

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 lower concentrations than required with other water-soluble polymers.

Range of product choices gives you the formulating versatility you need

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.

Two different chemical types

METHOCEL cellulose ether products are available in two basic types: Methylcellulose and hydroxypropyl methylcellulose. Both are made by the reaction of wood or cotton cellulose fibers with chemical reactants in the presence of caustic soda. The fibrous reaction product is purified and ground to a fine, uniform powder.

Methylcellulose is made using methyl chloride. These are METHOCEL A brand products. Hydroxypropyl methylcellulose products are made using propylene oxide and methyl chloride. These are METHOCEL E, F, J, and K brand products. There are also special-grade METHOCEL products available that have been formulated to meet the requirements of specific industries.

Premium grades for food and drug applications

METHOCEL Premium 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).

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General properties common to the whole family of METHOCEL cellulose ether products are listed in this table. Individual METHOCEL products exhibit these properties to varying degrees, and may have additional properties desirable in specific applications. Detailed information on the performance properties of METHOCEL products can be found on pages 18-32.

Table 1: General properties of METHOCEL cellulose ethers

Water solubility. METHOCEL cellulose ethers dissolve in water with no sharp solubility limit. Surface-treated and granular METHOCEL products can be added directly to water systems. This feature provides exceptional handling flexibility and control of solubilization rate. While 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 12-17.

Organic solubility. Certain types and grades of METHOCEL 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 non-ionic 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 exhibit surfactancy in aqueous solutions to provide emulsification, protective colloid action, and phase stabilization. Surface tensions range from 42 to 56 dynes per cm.

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

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

Low taste and odor. Important in food and pharmaceutical applications.

pH stability. Stable over a pH range of 3.0-11.0.

Water retention. METHOCEL cellulose ethers are highly efficient water retention agents. This is valuable in food products, ceramics, and many other applications.

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

Film formation. METHOCEL products form clear, tough, flexible films that are excellent barriers to oils and greases. In food applications, this property is often utilized to retain moisture and prevent oil absorption during cooking.

Binding. Used as high performance binders for pigments, tobacco products, structured foods, pharmaceutical products, and ceramics.

Lubrication. Used to reduce friction in rubber, portland cement, and ceramic extrusions. Also used to improve pumpability of slurries such as stucco. In food applications, lubricity aids in extrusion and other forming processes.

Suspending. Used to control settling of solid particles (e.g., herbs and spices in salad dressings, solids in ceramic slips, and antacid suspensions).

Colloidal action. Used to prevent droplets from coalescing or agglomerating.

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

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Methylcellulose
METHOCEL A brand products

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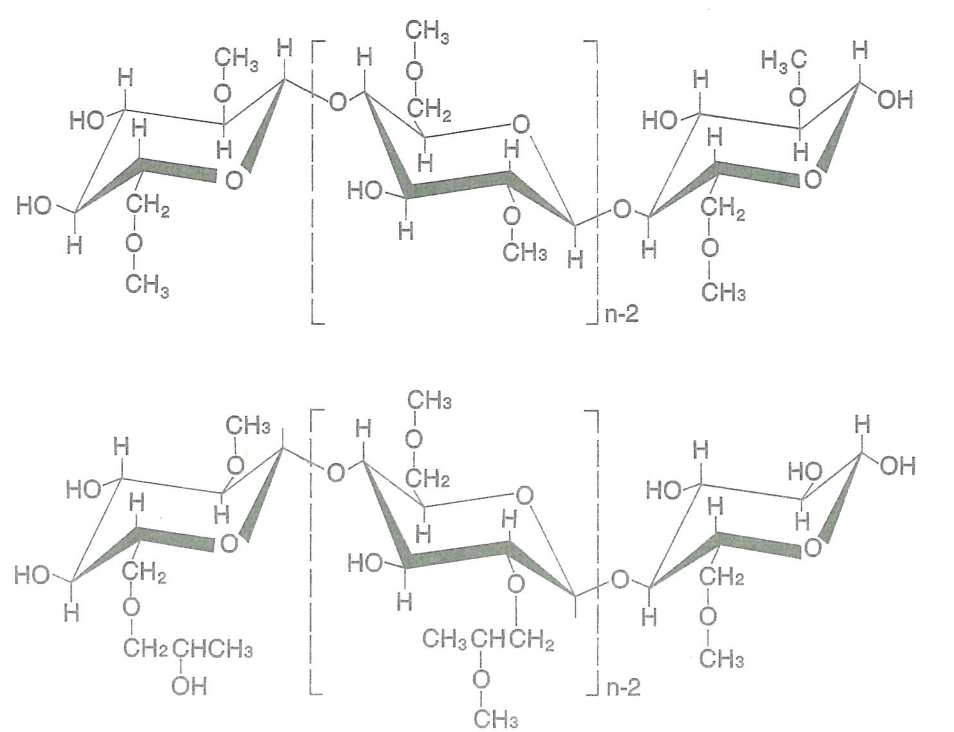
Hydroxypropyl Methylcellulose
METHOCEL E, METHOCEL F, METHOCEL J, & METHOCEL K brand products

All METHOCEL cellulose ether products have the polymeric backbone of cellulose, a natural carbohydrate that contains a basic repeating structure of anhydroglucose units. During the manufacture of cellulose ethers, cellulose fibers are treated with caustic solution which in turn is treated with methyl chloride, yielding the methyl ether of cellulose.

For hydroxypropyl methylcellulose products, propylene oxide is used in addition to methyl chloride to obtain hydroxypropyl substitution on the anhydroglucose units. This substituent group, $-OCH_2CH(OH)CH_3$, 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.

Figure 1: Typical chemical structures of METHOCEL products



Viscosity grades from 3 to 100,000 mPa•s

METHOCEL cellulose ether products are available in various viscosity grades, ranging from 3 to 100,000 mPa•s**. Since the viscosity of a solution depends on the concentration of METHOCEL, this wide range of product viscosities allows you to obtain the viscosity you want in a formulation while using a concentration that gives the desired level of other performance properties.

***Note: mPa•s (millipascal-seconds) is equivalent to cP (centipoise). All solution viscosities are measured with Ubbelohde viscometers at a 2 percent concentration in water at 20°C (68°F).*

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 water systems.

Techniques commonly used in preparing solutions with different physical forms of METHOCEL products are summarized on pages 12-17 of this handbook.

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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.*

***Note:** There are also a number of special purpose METHOCEL products developed for cosmetics, pharmaceuticals, ceramics, and other applications which have different systems of nomenclature (e.g. METHOCEL 40-Series products, a family of special surface-treated products for cosmetic formulations).*

Key to product nomenclature for METHOCEL products

METHOCEL is a trademark of The Dow Chemical Company for a line of cellulose ether products. In identifying many individual METHOCEL 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. The letter "C" is frequently used to represent 100, and the letter "M" is used to represent 1000 in designating viscosity.

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 "Surface-treated" products.

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 are 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 your local Dow sales office or by calling our toll-free number, 1-800-258-2436. Literature covering the use of METHOCEL products in many of the applications listed on pages 6-9 of this handbook is also available on request. Just call 1-800-258-2436, tell us what types of formulations or products you are working on, and we'll send you all the current literature that applies.

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 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.

Call 1-800-258-2436. Ask for extension 26/METHOCEL

Again, if you would like samples, additional literature, or technical assistance, don't hesitate to call. Call your local Dow sales office listed on the back cover of this brochure, or use the toll-free number. Call today. The sooner you get started formulating with METHOCEL, the sooner you'll start seeing improved performance and economy in your products.

Applications for METHOCEL cellulose ethers

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The seemingly 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 your local Dow sales office or call us toll-free at 1-800-258-2436.

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Adhesives

Carpet backsizing compounds – METHOCEL imparts 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 – Used to paste hides to smooth porcelain or glass surfaces in leather drying processes. Due to water retention efficiency and thermal gelation, METHOCEL proves much more effective than starch based pastes.

Plywood laminating adhesives – Used to control viscosities in glues for plywood manufacture. Thermal gelation and thickening properties 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 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 is used as a thickener in a variety of latex adhesives (e.g., 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 – Used as a suspending and dispersing aid for wettable pesticide and fertilizer powders. Provides 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 effectively bind pesticides, innoculants, and nutrients to seeds. METHOCEL products feature low plant toxicity and won't harm germinating plants.

Ceramics Processing

Tape casting – Provides better flow and leveling, and more uniform thicknesses. Low sodium residues provide 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 ether allows precise control of rheology in ceramic mixes, permitting broader operating ranges. Lubricity reduces energy consumption and die wear, promotes smoother surfaces. Thermal gelation permits extrusion of extremely delicate, thin walled shapes without sagging or deformation.

Dry and isostatic pressing – METHOCEL provides 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 – Improves control of viscosity and rheology. In addition, METHOCEL cellulose ethers fire out completely in the kiln.

Injection molding – Provides higher green densities and better green strength.

High temperature coatings/refractory mixes and mortars – Improves workability and application properties. Low ionic salt residues won't lower melting points. Can permit a reduction in use of low melting point plasticizers.

Chemical Specialties

Resins – METHOCEL is 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 – 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 – Used in PVC polymerization as a primary and secondary suspension agent. Provides excellent particle size control, good porosity for improved plasticizer absorption, low reactor scaling, and high bulk densities.

Construction Products

Dry wall tape joint compounds – Used to 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.

Tile mortars – METHOCEL provides water retention and workability to portland cement based ceramic tile mortars. Also improves adhesion, reduces skinning, and increases open time.

Masonry mortars – Used as a performance additive in masonry mortars, METHOCEL extends board life and improves workability. METHOCEL also contributes to air entrainment, often reducing the need for other additives for this purpose.

Wall and ceiling textures – Imparts pumpability, adhesion, workability; and water retention in wall and ceiling texturizing products.

Cement plaster and stucco – METHOCEL cellulose ether provides 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.

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

Frozen desserts – Modified ice crystal size gives smoother texture, improved emulsion stability. Increased air entrainment improves overrun.

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

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 Premium food gums 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 shelf life. Solids stay in suspension longer and control over body and pouring characteristics is improved.

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 – Provides viscosity control, cling, foaming, soil antiredeposition, and emulsion stabilization to household cleaners and detergents.

Paints

Latex paints – Used as a thickener in latex paints. Provides 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.

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. 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

Greaseproof coatings, release coatings, and surface sizings – Grease and oil barrier properties in conjunction with film forming abilities make METHOCEL valuable in a variety of paper coatings and sizings. The high film tensile strength and good elongation properties offered by METHOCEL play key roles in these applications.

Personal Care Products

Shampoos – METHOCEL cellulose ether is widely used as a thickener in shampoos. Since the thickener 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.

Creams and lotions – METHOCEL can contribute film forming and secondary thickening properties which improve afterfeel and other sensory characteristics in creams and lotions.

Pharmaceuticals

Tablet coatings – METHOCEL cellulose ethers form strong films with good adhesion. They provide a taste masking film 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 produces hard tablets with low friability, yet won't negatively affect tablet disintegration. METHOCEL allows the reduction of compression force, an important factor in extending the life of tooling and equipment.

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Controlled release – METHOCEL cellulose ether can be used for controlled release pharmaceuticals using two different methods: 1) METHOCEL can be used in a hydrophilic matrix tablet or capsule as described in a separate bulletin on sustained release.
2) METHOCEL is also 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, multi-particulate delivery such as extruded beads or chips, implants, 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.

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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, strengthening 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

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, and methylcellulose may be used in formulations applied to animals. Both Standard and Premium grade METHOCEL cellulose ether products are appropriate.

Pharmaceuticals

Premium grades of METHOCEL A, METHOCEL E, METHOCEL F, and METHOCEL K products are used for pharmaceutical and topical applications. Methylcellulose and hydroxypropyl methylcellulose are listed in USP XXI. In addition, methylcellulose (METHOCEL A products) is Generally Recognized As Safe (GRAS) by the Food and Drug Administration.

To support new drug applications, master files for these products are on file at the Bureau of Drugs of the Food and Drug Administration. Permission to open the master file can be obtained by writing:

The Dow Chemical Company
Product Safety & Compliance
2030 Dow Center
Midland, MI 48674

Note! The Dow Chemical Company advises against the use of METHOCEL cellulose ether products in any form in the preparation of parenteral or intravenous injections, because the material is not readily metabolized. Significant injury to the kidney may result from impurities in the blood stream, especially if the methylcellulose had not been properly dissolved.

A bibliography of pharmaceutical and medical references is available from:

The Dow Chemical Company
Chemicals and Performance
Products Department
2020 Dow Center
Midland, MI 48674

Foods

The properties of METHOCEL Premium cellulose ethers have long been used in the food industry. 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 according to 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 METHOCEL products are approved for direct food use, they can be used as packaging components and in indirect applications for food use. Premium grade METHOCEL products meet the specifications of the United States Pharmacopeia (USP) and the Food Chemicals Codex (FCC). Premium grade METHOCEL products are also available which meet the European Pharmacopeia (EP) and the Japanese Pharmacopeia (JP).

****METHOCEL J products are not cleared under this regulation.*

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When labeling these food ingredients, one can take advantage of either their proper chemical names or their common or usual 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 year round and Passover use by the Union of Orthodox Jewish Congregations of America.

METHOCEL Premium products are approved for use in the European Economic Community (EEC) and have E number status. The EEC allows methylcellulose (E461) and hydroxypropyl methylcellulose (E464) for broad food use. However, the regulations for specific food ingredients vary from country to country. Please contact us for the status of specific applications.

EPA/TSCA compliance

In compliance with EPA regulations, all Dow sales items subject to the reporting requirements have been reported to the Administrator of the Environmental Protection Agency for inclusion in the inventory of existing commercial chemical substances under Section 8 (b) (1) of the Toxic Substances Control Act PL94-469 (15 USC 2601 et seg.). Where the product consists of a mixture, we will assure that the individual chemicals were reported. The Chemical Abstracts Services Registry No. (CAS) is 9004-67-5 for methylcellulose and 9904-65-3 for hydroxypropyl methylcellulose.

How to prepare solutions of METHOCEL

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 low viscosity products can be made at 10-15% concentration. High viscosity products find a normal limit at 2-3% concentration.

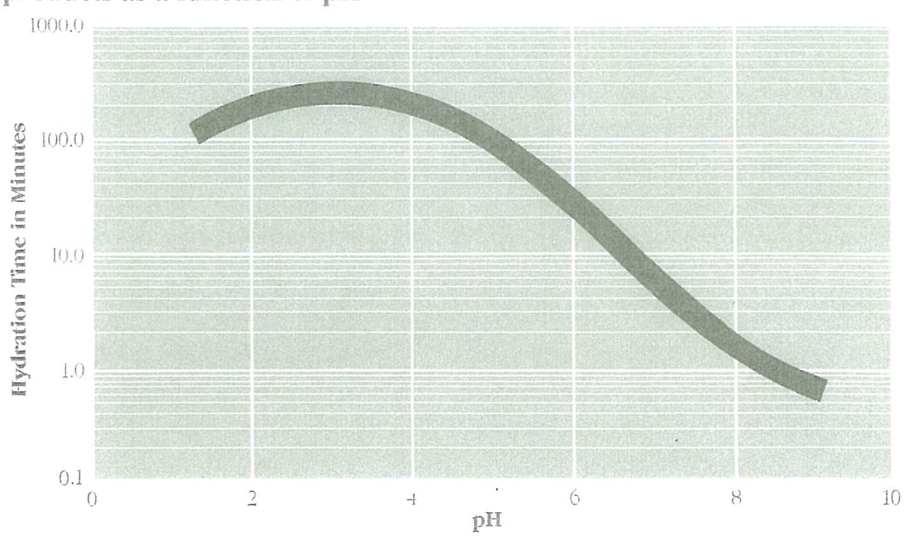
The form of METHOCEL cellulose ether product chosen (powder or surface-treated powder) influences the techniques used in making solutions. Surface-treated and granular products can be directly added to water systems. They disperse readily with mild agitation and dissolve (build viscosity) gradually under neutral conditions. The dissolution rate of surface-treated products can be increased by adjustment to an alkline pH after dispersing the powder in water. While 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 initial level of 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 (relative to water in the system) exceeds 5% by weight. 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.

Figure 2: Typical hydration delay time of surface-treated METHOCEL® products as a function of pH



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In many cases it is desirable to "trigger" viscosity build immediately following dispersion. This can conveniently be done by adding a small amount of a base such as ammonium hydroxide, sodium bicarbonate, etc. If the METHOCEL product is dispersed in neutral (pH approximately 7) water 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 8.5-10.0 with continued agitation until full viscosity is reached (usually 10-30 minutes).

Working with untreated powders

While 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 in ambient temperature or cold water by using an eductor funnel or high-shear 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, forming a gelatinous membrane which shields the remainder from complete hydration. Several dispersion techniques are commonly used, each with 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 required total volume of water heated 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.

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

Since complete hydration depends on adequate cooling, METHOCEL E, F, J, and K brand products are frequently used in applications where low temperature water is not available. Figure 3 illustrates the effects of cooling hot slurries of METHOCEL A and METHOCEL K products.

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.

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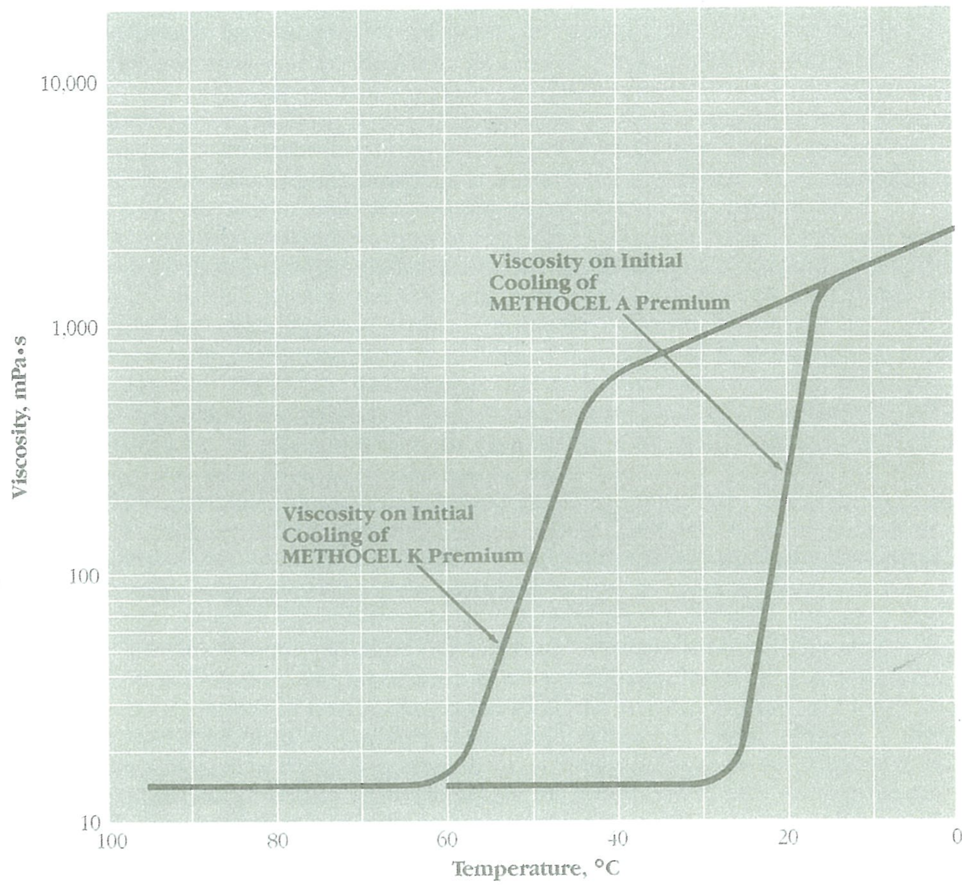
This figure illustrates that a slurry of METHOCEL K brand cellulose ether (HPMC) requires much less cooling for hydration than a slurry of METHOCEL A cellulose ether (MC). Slurries of METHOCEL E and F and J brand products also require less cooling than METHOCEL A brand products.

Figure 3: Viscosity development of METHOCEL® A and METHOCEL K brand products slurried at 2% in hot water



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.

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 5-8 parts non-solvent to 1 part METHOCEL is recommended to obtain a fluid slurry.

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

Solubility in non-aqueous solvents

The solubility of METHOCEL cellulose ethers in non-aqueous media varies according to the nature and quantity of substituent groups on the anhydroglucose chain. METHOCEL E or 310-Series products are generally recommended where solubility in, or compatibility with, non-aqueous media is desired.

Note: Since surface-treated METHOCEL products are designed to control dispersibility and solubility rate in aqueous media, they should not be used in non-aqueous media.

Because METHOCEL products are soluble in water, their solubility in non-aqueous solvents offers

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unique dual solubility. This feature has proven valuable in pharmaceutical tablet manufacture where the use of non-aqueous coating systems to apply water-soluble films to tablets has substantially improved processing economy.

Solvent solubility at elevated temperatures

In general, binary solvent systems function more effectively with METHOCEL products than single solvents. Where alcohols comprise part of the binary solvent, solvent power improves as the molecular weight of the alcohol decreases. Methanol therefore performs very well. Table 2 lists several compounds which are typical of the types of solvents that can be used with certain METHOCEL cellulose ether products.

Table 2: Typical non-aqueous solvents used with METHOCEL® cellulose ethers

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

Four dispersion techniques, step-by-step

→
While METHOCEL powders are soluble in cold water, they must be thoroughly dispersed in the water before they begin to dissolve. If you add METHOCEL powders directly to cold water, you'll get a lumpy solution – unless you are using surface treated powders. Each of the four procedures described here has advantages in certain applications. More detailed information on each procedure is provided on pages 12-15.

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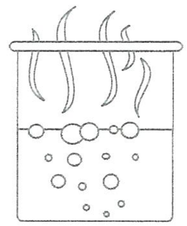
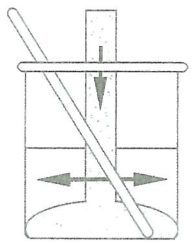
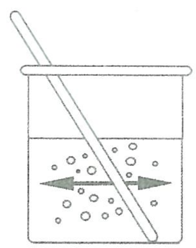
Dispersion in hot water



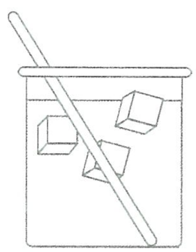
1. Heat approximately 1/3 the required volume of water to at least 194°F (90°C).



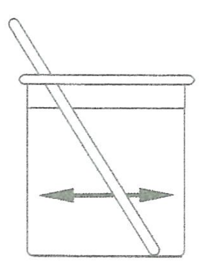
2. Add the METHOCEL powder to the heated water with agitation.



3. Agitate the mixture until the particles are thoroughly wetted and evenly dispersed.

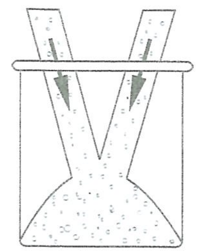


4. For complete solubilization, the remainder of the water is then added as cold water or ice to lower the temperature of the dispersion. Once the dispersion reaches the temperature at which that particular METHOCEL product becomes water-soluble, the powder begins to hydrate and viscosity increases. See page 13 for cooling times and temperatures for specific METHOCEL products.

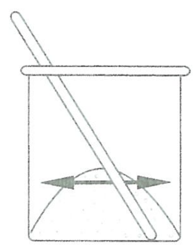


5. Continue agitation for at least 30 minutes after the proper temperature is reached. Your solution of METHOCEL cellulose ether is now ready for use.

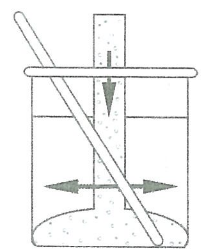
Dry blending



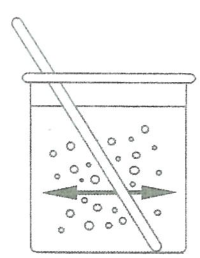
1. Combine METHOCEL powder with other dry powdered ingredients. The suggested ratio of other dry powdered ingredients to METHOCEL is 7:1. The minimum ratio of other dry powdered ingredients to METHOCEL powder may vary from 7:1 to 3:1.



2. Thoroughly blend the dry components.

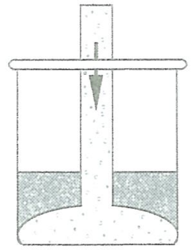


3. Add the dry mix to the water with agitation. The rate of hydration will depend upon both the relative particle sizes and the rate of agitation during and after addition of the mixture to the water.

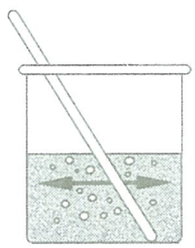


4. Agitate until the METHOCEL powder has completely hydrated and the solution is consistently smooth. Your solution of METHOCEL cellulose ether is now ready for further processing.

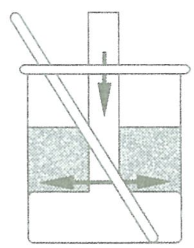
Dispersion in non-solvent media



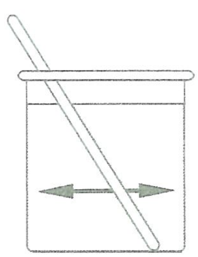
1. METHOCEL cellulose ethers may also be dispersed in non-solvent media such as vegetable oil, propylene glycol, polyethylene glycol, concentrated salt solutions, glycerine, corn syrup, and high fructose corn syrup. A ratio of 5-8 parts non-solvent to 1 part METHOCEL is recommended to obtain a liquid slurry.



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



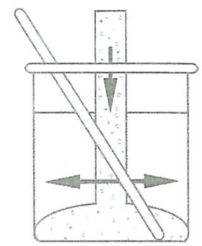
3. The dispersion of METHOCEL in non-solvent medium may be added to cold water, or the cold water may be added to the dispersion.



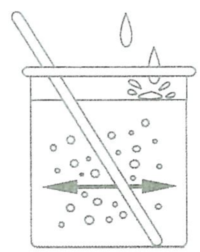
4. Continue mixing until the METHOCEL powder is completely hydrated and the solution is smooth. You can now add the remaining ingredients in your formulation.

Dispersion of surface-treated powders

The surface-treated powders of METHOCEL cellulose ether products are added directly to water systems. Such powder products will disperse readily with mild agitation and are dissolved (build viscosity) when made alkaline. The hydration of these products has been inhibited in a manner that permits the use of pH to control the point at which solubilization occurs.



1. Add the surface-treated METHOCEL powder to the water. Begin agitation.



2. Continue agitation and add sufficient ammonium hydroxide, sodium bicarbonate, or other alkaline material to the dispersion to obtain a pH of 8.5-9.0. This will result in rapid viscosity development. Continue agitation until sufficient hydration has been achieved.

Properties of METHOCEL powders

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/cc.

Moisture sorption

METHOCEL products sealed in their original shipping containers absorb little to no atmospheric moisture. Once a container is opened, however, there is pick-up 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 assure using the proper weight of METHOCEL to give the viscosity desired.

To minimize moisture pick-up, 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.

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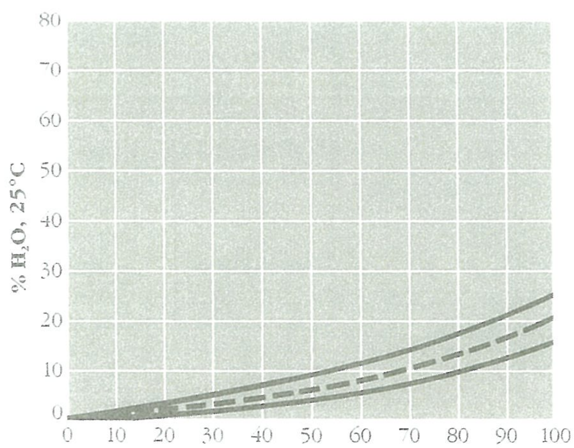
Figure 4: Equilibrium moisture content vs percent relative humidity, 25°C



Properties of solutions of METHOCEL

Table 3: 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 n_D^{20}

Partial specific volume

4,000 mPa•s METHOCEL A .... 0.725 cc/g (0.087 gal/lb)
4,000 mPa•s METHOCEL E .... 0.767 cc/g (0.092 gal/lb)
4,000 mPa•s METHOCEL F .... 0.734 cc/g (0.087 gal/lb)
5,000 mPa•s METHOCEL J .... 0.725 cc/g (0.087 gal/lb)
4,000 mPa•s METHOCEL K .... 0.717 cc/g (0.086 gal/lb)
15,000 mPa•s METHOCEL K .... 0.724 cc/g (0.087 gal/lb)

Freezing point, 2% solutions, all types

0.0°C at 2% concentration

Surface tension, 25°C, 0.05% concentrations

Water .... 72-74 x 10^{-3} Newton/meter (72-74 dynes/cm)
Methylcellulose .... 53-59 x 10^{-3} Newton/meter (53-59 dynes/cm)
Hydroxypropyl methylcellulose ...... 43-55 x 10^{-3} Newton/meter (43-55 dynes/cm)

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 (e.g., paints, cosmetics, food 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, at a temperature below the incipient gelation temperature (see pp. 27-28), aqueous solutions of METHOCEL exhibit pseudoplastic flow. 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.

→

Note: Numbers on curves indicate viscosity types.

Figure 5: Apparent viscosity vs. shear rate, 2% aqueous solutions, 20 °C

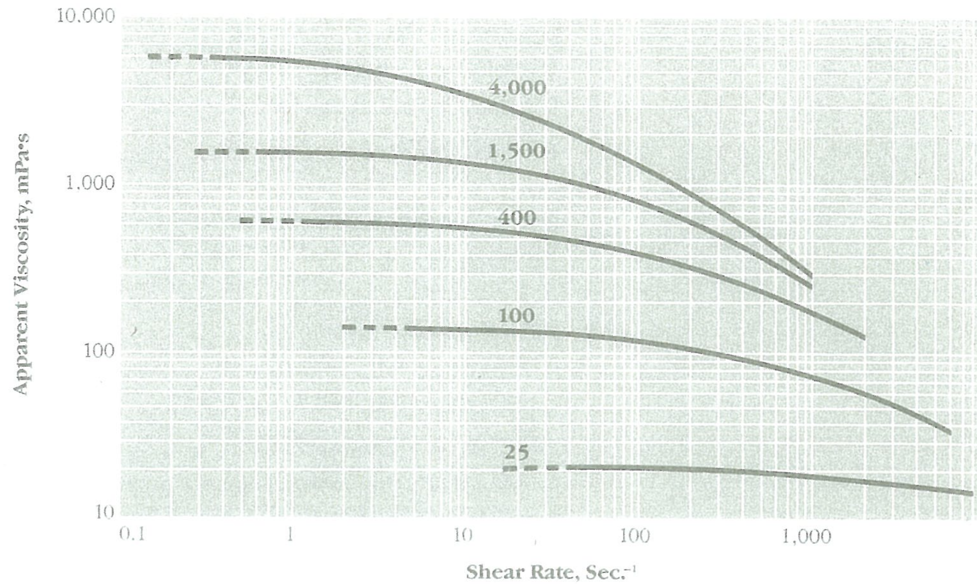
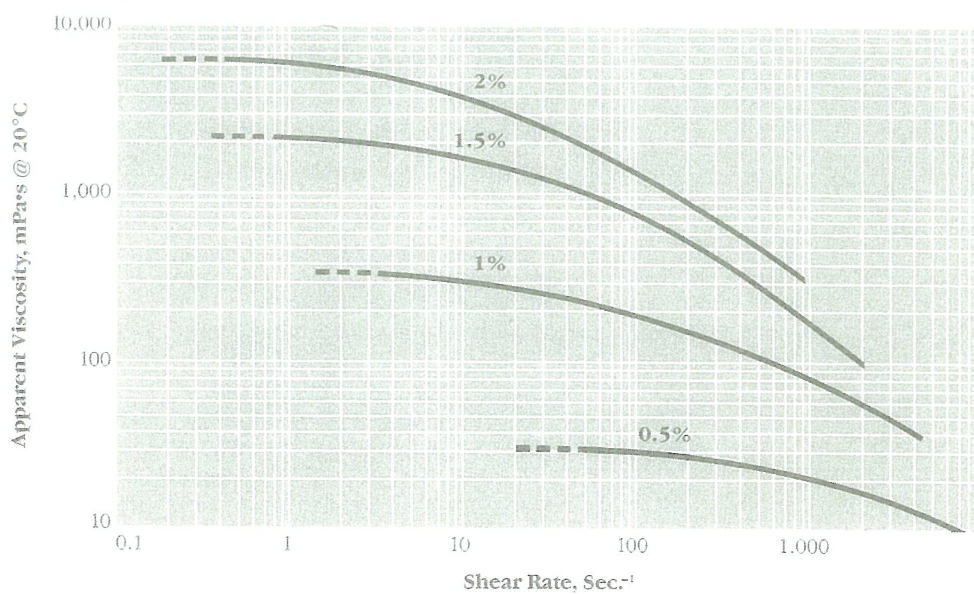


Figure 6: Apparent viscosity vs. shear rate for aqueous solutions of 4,000 mPa•s METHOCEL® at various concentrations



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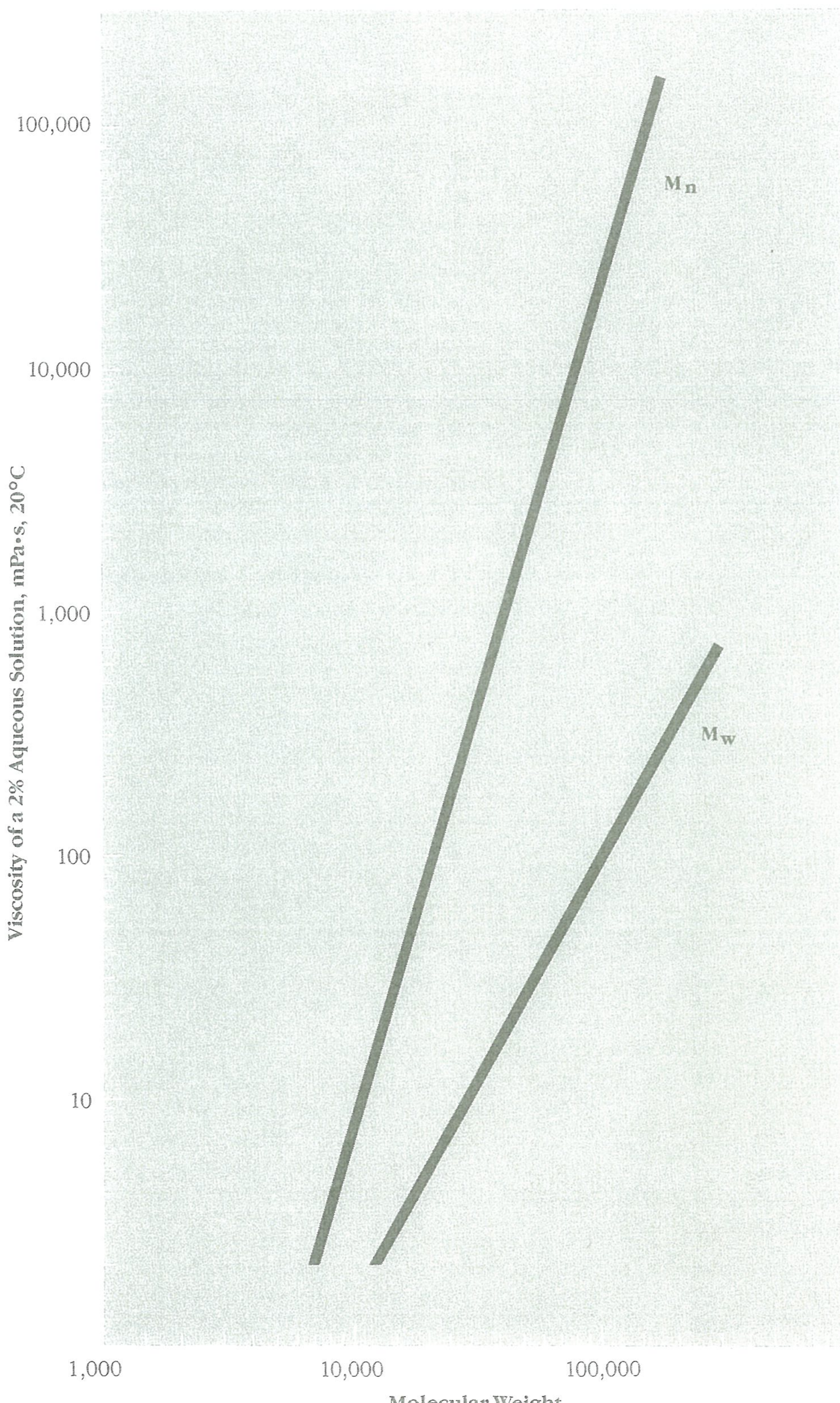
Molecular weight/viscosity relationships

The apparent viscosity of aqueous solutions of METHOCEL 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 (M_n) and the commercial viscosity designation for METHOCEL A cellulose ethers is shown in figure 7.

→

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 (M_n)*** *is calculated from the limiting osmotic pressure of the solvent as the concentration of the solute approaches zero. The* ***Weight Average Molecular Weight (M_w)*** *will be 3-10 times the M_n.*

Figure 7: Molecular weight/viscosity correlation, 20°C



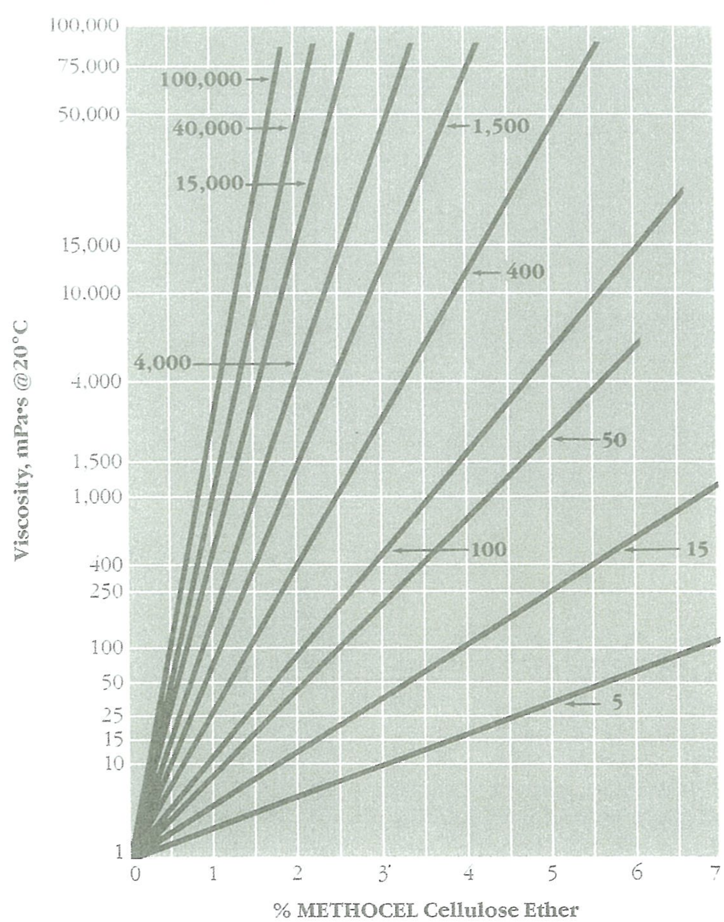
Effect of concentration on viscosity

Most formulations require a predetermined product viscosity of METHOCEL cellulose ether. Figure 8 shows how the concentration of the various viscosity METHOCEL products affects 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. This graph is plotted on 8th root, not on logarithmic paper. 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 $\eta^{1/8} = (C \bullet \alpha) + 1$, 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, $(4{,}000)^{1/8} = (C \bullet \alpha) + 1$ and solving for α yields a value of 0.910. For a 1500 mPa•s product, $(1500)^{1/8} = (C \bullet \alpha) + 1$ and solving for α yields a value of 0.747. Having calculated α for a particular METHOCEL product, this value can be used to calculate viscosities at other concentrations.

Figure 8: Viscosity/concentration relationships



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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.

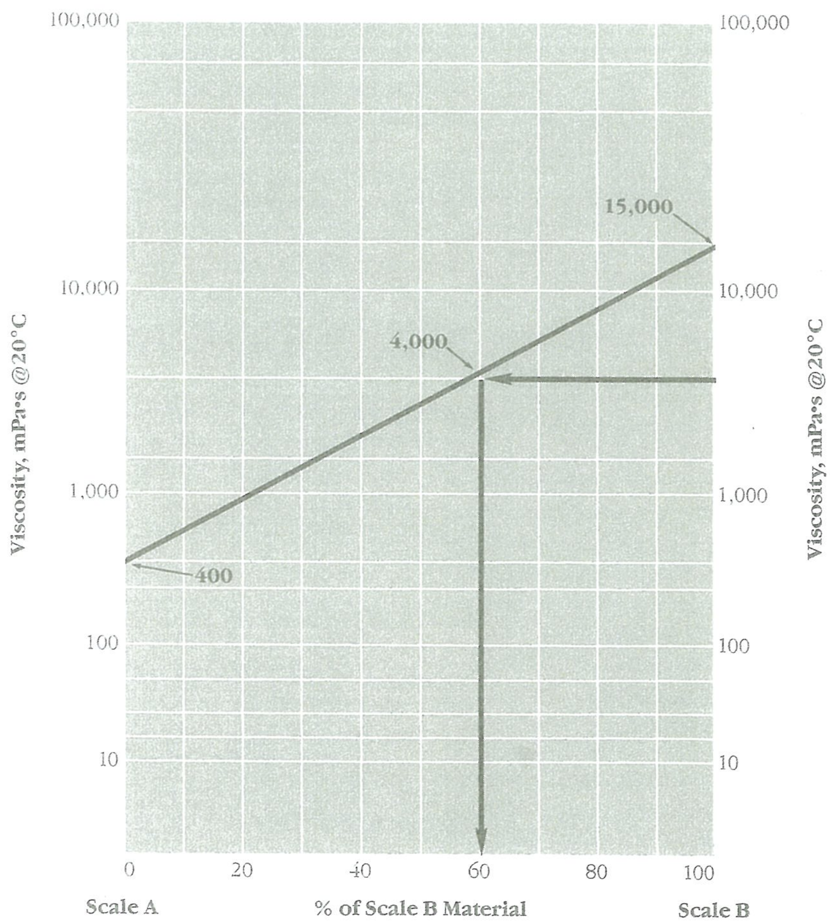
To use the chart, the points corresponding to the viscosities of the two starting materials are selected on the two vertical scales (A and B) and connected with a line. The point corresponding to the desired final viscosity is then located on one of the vertical scales and a horizontal line drawn from it to the first line drawn. A vertical line drawn from this intersection to the bottom scale will reveal the percent of right hand (Scale B) material needed to make up the blend.

This 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.

Figure 9: Blending chart



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 those gums which 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 longer 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 which is dependent on the concentration of the interacting materials and on the presence of other ingredients such as pigments, latex particles, or preservatives. 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.

Defoamers for aqueous solutions

The foaming of solutions of METHOCEL cellulose ether is easily controlled by using foam stabilizers and defoamers. Table 4 lists several defoamers which have proven effective. However, other commercial defoamers may work equally well and all products should be tested for performance.

The concentration required for defoaming with any of the listed agents is 25-1000 ppm, based on solution weights. 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.

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Table 4: Defoamers for aqueous solutions

Application	Defoamer	Producer
General use	Colloids 581 B	Colloids, Inc.
	Nopco KFS	Henkel, Process Chemical Division
	Antifoam A, B, C	Dow Corning Corporation
	Lauryl alcohol	Dow Corning Corporation
	Polyglycol P1200	The Dow Chemical Company
Paper sizings	Colloids 770	Colloids, Inc.
Latex paints	Foamaster 111, VF, G, R	Henkel, Process Chemical Division
	Nopco NXZ	Henkel, Process Chemical Division
	Colloids 643	Colloids, Inc.
	Drew 475	Drew Chemical, Division of Ashland Chemical
Foods	Dow Corning FG-10	Dow Corning Corporation
	Foamaster 6-FG	Henkel, Process Chemical Division

Resistance to microorganisms

An important property of METHOCEL cellulose ethers is their high resistance to attack by microorganisms. The fact that virtually all METHOCEL methylcellulose and METHOCEL hydroxypropyl methylcellulose passes through the intestinal tract essentially unchanged attests to the stability of these products to a wide range of biochemical and enzymatic systems.

As the cellulose is modified by substitution with various radicals, such as alkyl and hydroxyalkyl groups, resistance to microbial attack increases. The degree of substitution (D.S.) is 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, and a D.S. of well above 1.0, they possess excellent resistance to microbial attack.

The higher substitutions of the METHOCEL J brand products are especially resistant to enzymes. Maintenance of shelf life in paints and other latex-based coatings, and stability in a range of solutions and other products containing METHOCEL are greatly increased by this resistance to microorganisms.

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 0.05-0.1% of DOWICIDE* A antimicrobial or DOWICIL* 75 preservative is suggested. More information on these products is available on request. For regulated uses, you should use the appropriate permitted preservative.

*Trademark of The Dow Chemical Company

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, and K brand hydroxypropyl methylcellulose products generally exhibit a higher tolerance for salts in solution than METHOCEL A brand methylcellulose products. There is only slight variation in electrolyte tolerance among the various METHOCEL hydroxypropyl methylcellulose products (Table 5).

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. Since 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.

Table 5: Grams of additive tolerated by 100 cc, 2% solutions, 20°C METHOCEL® Products

Additive	A15-LV	A4M	E15-LV	F50	F4M	K100-LV	K4M	J5MS
NaCl	24	11	22	15	15	19	16	19
$MgCl_2$	11	8	30	35	25	40	39	22
Na_2SO_4	11	4	12	9	4	6	4	6
$Al_2(SO_4)_3$	11	7	7	7	7	8	8	7
Na_2CO_3	4	3	7	5	4	5	5	7
Na_3PO_4	10	6	10	11	6	11	11	9
Sucrose	100	65	80	120	80	160	115	100

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Thermal gelation in aqueous media

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 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.

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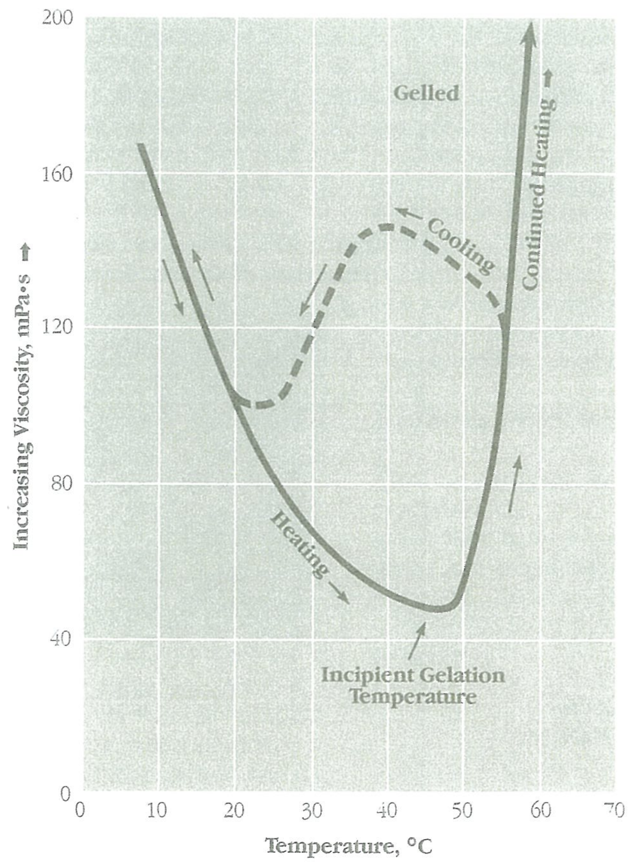
Gelation of a 2% aqueous solution of METHOCEL A100 Methylcellulose. Heating rate, 0.25°C/min.

Figure 10: Thermal gelation of methylcellulose



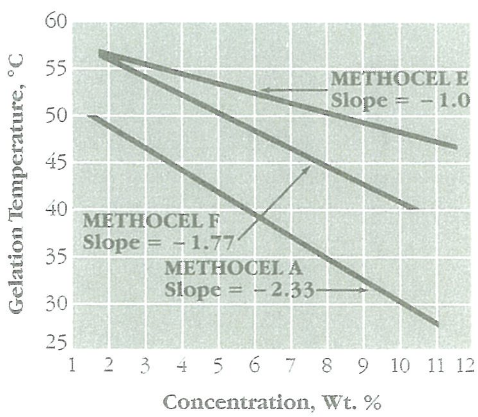
Controlling gel temperature

The specific temperature at which bulk thermal gelation occurs (the incipient gelation temperature or IGT) and the firmness of the gel is governed by the nature and quantity of the substituent groups attached to the anhydroglucose ring and thus varies with each type of cellulose ether (Table 6). 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.

Table 6: Gel temperatures and structures

METHOCEL product type	Approximate gel point (2% aqueous solutions)	Gel structure
A	50-55°C	Firm
E	58-64°C	Semi-firm
F	62-68°C	Semi-firm
K	70-90°C	Soft

Figure 11: Gelation temperature as a function of concentration



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, F or E type METHOCEL 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 on increasing molecular weight and gradually becomes constant at or above a viscosity grade of 400 mPa•s. Gel strength also increases with increasing concentration.

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

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.

As a specific example, a 0.01 wt% solution of METHOCEL A15-LV 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.

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. While 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 a gel point raising additive 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 13°C.

The increase in the thermal gel point is directly proportional to the increase in concentration of the gel point raising 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

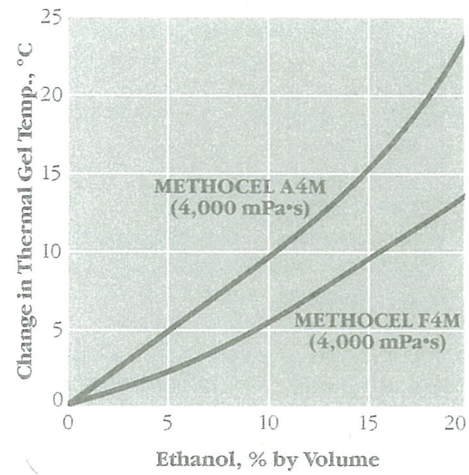
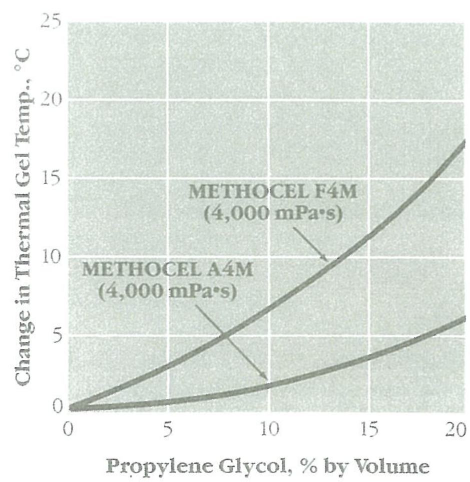


Figure 13: Effect of propylene glycol on gel temperature, 2% solutions



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Properties of films of METHOCEL

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 7. 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 crosslinking compounds and resins. The degree of insolubility can be controlled by the choice and quantity of crosslinking 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.

Table 7: Properties of unplasticized films of METHOCEL®

Properties[1]	METHOCEL A15-LV	METHOCEL E15-LV
Specific gravity	1.39	1.29
Area factor	24,000 in^2/lb/mil	25,860 in^2/lb/mil
Moisture vapor transmission rate, 100°F, 50% RH	67.5 g/100 in^2/24 hr/mil	65 g/100 in^2/24 hr/mil
Oxygen transmission rate, 75°F	25 cc/100 in^2/24 hr/mil	70 cc/100 in^2/24 hr/mil
Tensile strength, 75°F, 50% RH	9,000 lbs/in^2 ± 10%	10,000 lbs/in^2 ± 10%
Elongation, 75°F, 50% RH	5-15%	5-15%
Stability to ultraviolet light, 500 hrs, Fadeometer exposure	Excellent	Excellent
Resistance to oils and most solvents	Excellent	Excellent
Ultraviolet transmission,		
400 nm	55%	82%
(2 mil film) 290 nm	49%	34%
210 nm	26%	6%

[1]Typical properties, not to be construed as sales specifications. Data based on a 1 mil dry film.

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 80-160°C (176-320°F). Properly plasticized sheet and tubing of METHOCEL cellulose ether can be heat-sealed at about 130°C (266°F).

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Analytical Methods

Measuring Viscosity

Certain precautions must be observed for the accurate measurement of the viscosity of solutions of METHOCEL since they exhibit a non-linear shear stress/shear rate relationship which results in pseudoplastic viscosity behavior at most shear rates (see pp. 19-20).

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 50-150 seconds (see Table 8). 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 millipascal-seconds (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.

Table 8: Capillary tubes for measuring viscosity

Viscosity, mPa•s	Size of heavy wall tubing, inside diameter	
15	1.5mm	**Low**
100	2.4mm	**Viscosities**
400	3.2mm	
1,500	5.0mm	
4,000	6.0mm	
8,000	7.5mm	**High**
15,000	10.0mm	**Viscosities**
50,000	15.0mm	
75,000	15.0mm	

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.

*****Brookfield Synchro-lectric viscometer, Brookfield Engineering Co., Stoughton, Massachusetts.*

Published analytical methods

Procedures for the analysis of METHOCEL cellulose ether products have been standardized under ASTM D1347 and ASTM D2363. These and other information on analysis are listed in the following references.

Methods for Testing Methylcellulose – Current ASTM D1347, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

Methods for Testing Hydroxypropyl Methylcellulose – Current ASTM D2363, 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-11A, (1973).

Application of Anthrone Test to Determination of Cellulose Derivatives in Non-aqueous 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).

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Handling considerations

Material Safety Data Sheets for METHOCEL products are available from The Dow Chemical Company to help customers further satisfy their 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 necessarily general and are not a substitute for the detailed safety information found in the Material 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 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.

While 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. As a result, no special precautions need to be observed in order to handle the products safely.

Storage

METHOCEL products are organic polymers that will burn under the right conditions of heat and oxygen supply. Fires can be extinguished by conventional means.

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 135-145°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 74μ or less (finer than 200 mesh), critical levels are reached at concentrations of 28 gm/m^3(0.03 oz/ft^3). The minimum ignition energy required to cause a dust explosion is 0.030 Joules. Static from a human body has about 0.025 Joules. 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

While Dow studies using standard procedures showed no 5, 10, or 20 day BOD values, activated sludge studies with (^{14}C) 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.

Since 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 all federal, state, and local regulations are observed.* Dow recommends that the material be buried in an approved landfill; incineration should be done under carefully controlled conditions to avoid the possibility of a dust explosion.

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. Your Dow Sales Representative can arrange proper contacts.

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CHEMICALS AND PERFORMANCE PRODUCTS DEPARTMENT
MIDLAND, MICHIGAN 48674

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