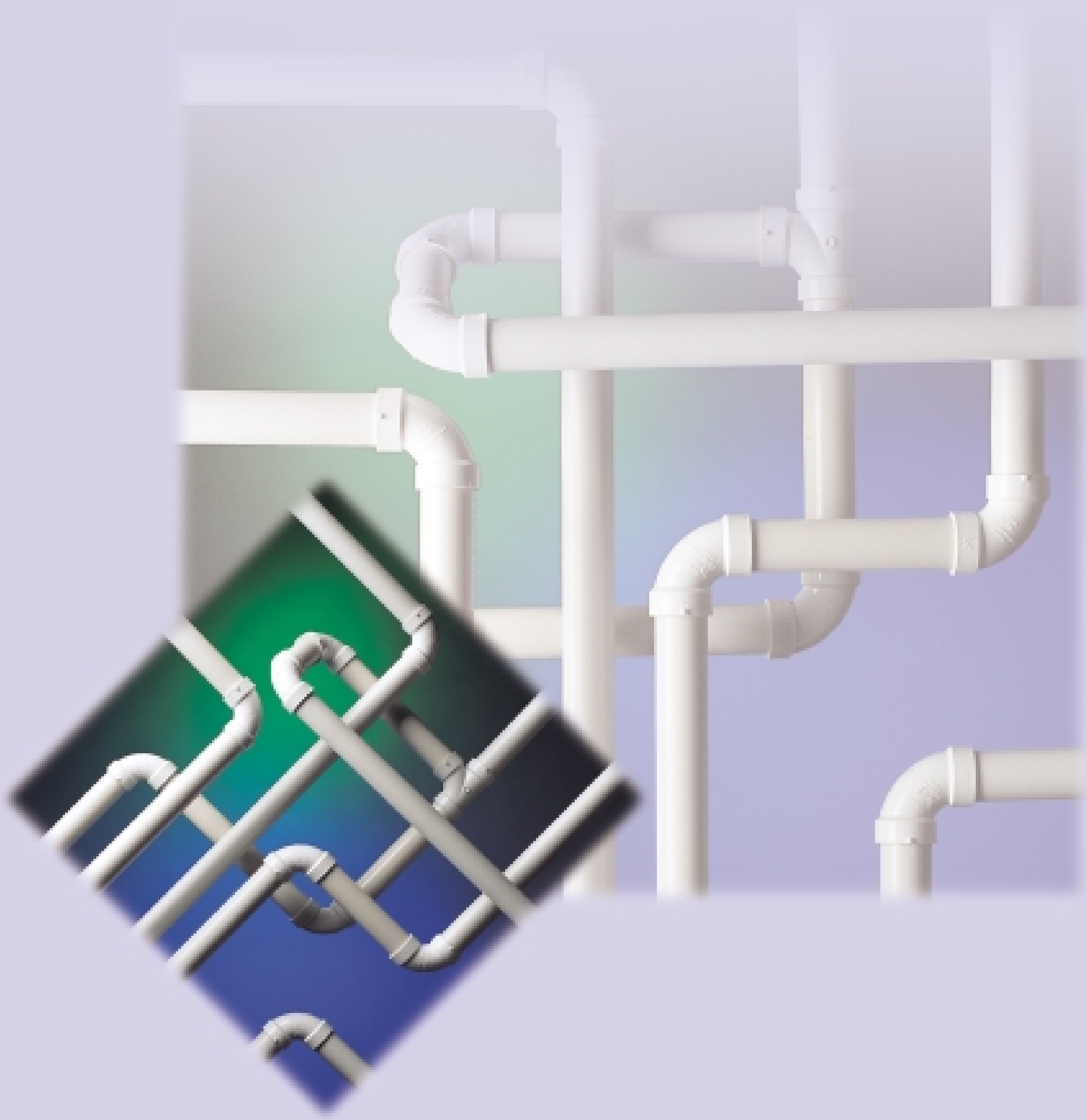
METHOCEL Cellulose Ethers as Suspending Agents for Suspension Polymerization of Vinyl Chloride



Introduction

An important characteristic of polyvinylchloride (PVC) is its ability to absorb additives, such as plasticizers, stabilizers, pigments, and impact modifiers, quickly and in sufficient quantities. However, the required level of porosity is often obtained at the expense of bulk density. Using the appropriate suspending agent during polymerization allows the producer to maintain a balance of these properties.

METHOCEL* cellulose ethers have been used for many years as suspending agents for vinyl chloride polymerization. These products are protective colloids made of linear polymers of condensed anhydroglucose rings that form a carbohydrate skeleton. Methyl and hydroxypropyl groups are attached to the carbohydrate skeleton via an ether linkage. METHOCEL cellulose ethers are nonionic, surface-active film formers. When used as suspending agents in vinyl chloride polymerization, they provide particle size control, uniform particle size distribution, and porosity that can be optimized for many PVC end-uses. This publication discusses the use of METHOCEL cellulose ethers as suspending agents for vinyl chloride polymerization.

Polyvinylchloride Particle Morphology

Suspension PVC is produced in different molecular weights (K-value), grain sizes, particle size distributions, and porosities. Grain diameters usually vary between 50 µm and 300 µm. The particle morphology is partly influenced by the polymerization conditions (temperature, reactor size, stirring conditions, cooling system, etc.). The largest influence, however, is given by the surface-active suspending agent.

In PVC suspension polymerization, vinyl chloride monomer is dispersed in water, forming small droplets. The use of a surface-active suspending agent (cellulose ether, polyvinyl alcohol, etc.) reduces the interfacial tension and facilitates dispersion. The suspending agent also reduces droplet size and forms a protective film, preventing the droplets from coalescing during polymerization.

Organosoluble radical initiators are usually added when the desired reaction temperature is reached. Polymerization starts both at the water/ monomer phase boundary and inside the droplet. At low conversion, polymerization occurs largely in the monomer phase following classic kinetics, where the rate of reaction is dependent on the square root of initiator concentration.

Because PVC is insoluble in its monomer, it precipitates, forming a swollen gel with the monomer. At higher conversion rates (5 to 65%), reaction kinetics become more complex because polymerization continues both in the monomer phase and in the gel phase. At conversions higher than 65%, no free monomer is left, and the viscosity of the gel increases rapidly while the remaining vinyl chloride monomer is consumed. At the same time, pressure drops in the reactor vessel. This is an indication that all free monomer has been polymerized. Polymerization is terminated at about 80 to 85% conversion, and the remaining vinyl chloride monomer is stripped off. Higher conversion rates would not be cost-effective.

Grain Size and Grain Size Distribution

Vinyl chloride monomer is dispersed in the aqueous phase prior to polymerization, forming spherical droplets of 30 to 40 µm diameter. During the course of reaction, the formation of polymer at the droplet surface reduces the ability of the protective colloid to prevent coalescence. The more sticky droplets aggregate in a controlled way, giving a final PVC resin with a grain size of 100 to 180 µm depending on the type of resin and the process conditions.

Porosity and Bulk Density

Porosity is a key parameter of PVC resins. Porosity determines the ease of removal of unreacted vinyl chloride monomer as well as the speed of plasticizer uptake. Porosity is largely influenced by the choice of an organosoluble secondary suspending agent. The balance of porosity and bulk density is a constant issue for the suspension PVC producer, who is striving for the best compromise.

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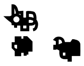
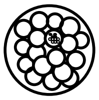
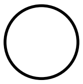
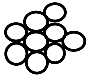
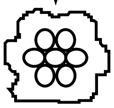
The morphology of the PVC grain is developed during the course of polymerization in a series of interrelated steps. Growth and stabilization of the microstructure within the vinyl chloride monomer droplet are the key factors for successful porosity control. Figure 1 shows a mechanism that has resulted from intensive research work and has found general acceptance in the PVC technical literature.

Vinyl chloride oligomers are insoluble in the monomer phase and have a chain length of more than ten units forming coiled macroradicals. These macroradicals fuse together to microdomains of 10 to 20 nm in diameter. These first stages occur at very low conversion rates of less than 1%. While polymerization continues, the microdomains become unstable and agglomerate to domains (0.1 to 0.2 µm) consisting of about 1000 microdomains. After these first aggregation steps the domains are quite stable and grow to primary particles of less than 1 µm diameter. No more domains are formed at this stage, and growth is based on precipitation of macroradicals on the domain surface and on polymer chain growth inside the polymer/ monomer gel phase. A third aggregation step follows where the domains form agglomerates of about 2 µm diameter at a conversion rate of less than 10%. These agglomerates grow within the droplet to a final size of about 5 µm.

The conversion of vinyl chloride monomer to PVC is accompanied by an increase in density from 0.85 g/cm^3 to 1.40 g/cm^3, producing a volume contraction of 39%. If the microstructure within the initial droplet is strong enough to withstand the contraction completely, PVC porosity could be as high as 39%.

Figure 1 – Mechanism for Growth of PVC Microstructure During Polymerization

Stage	Species	Microstructure	Percent Conversion	Size
Initiation R + vinyl chloride monomer	Coiled macroradicals		< 1	—
First aggregation step	Microdomains (about 50 microradicals)		1 - 2	10 - 20 nm
Second aggregation step	Domain - primary nucleus (about 1000 microdomains)			0.1 - 0.2 µm
Growth	Primary particle		4 - 10	0.6 - 0.8 µm
Third aggregation step	Agglomerate			1 - 2 µm
Growth	Fused agglomerate		90	2 - 10 µm

METHOCEL Cellulose Ethers

Nomenclature and Physical Properties

METHOCEL is a registered trademark of The Dow Chemical Company for its cellulose ether products. The first letter of the product designation specifies the chemistry of the cellulose ether. “A” indicates all methylcellulose products; “E,” “F,” “K,” and “J” indicate hydroxypropyl methylcellulose products of different substitution levels. The number that follows a letter specifies the viscosity of a 2% aqueous solution. For example, METHOCEL K100 cellulose ether is a hydroxypropyl methylcellulose with 23% methoxy substitution and 6.5% hydroxypropyl substitution where a 2% aqueous solution has a viscosity of 80 to 120 mPa·s.

Low-viscosity hydroxypropyl methylcellulose ethers are the most suitable cellulose ethers for PVC polymerization. The level of substitution with methoxy and hydroxypropyl groups and the aqueous viscosity determines the performance characteristics as a PVC suspending agent. Figure 2 gives an overview of chemistries of METHOCEL cellulose ethers within the matrix of substitution and nomenclature. Table 1 shows the range of METHOCEL products for the suspension-PVC market and their properties.

Figure 2 – Overview of METHOCEL Chemistry

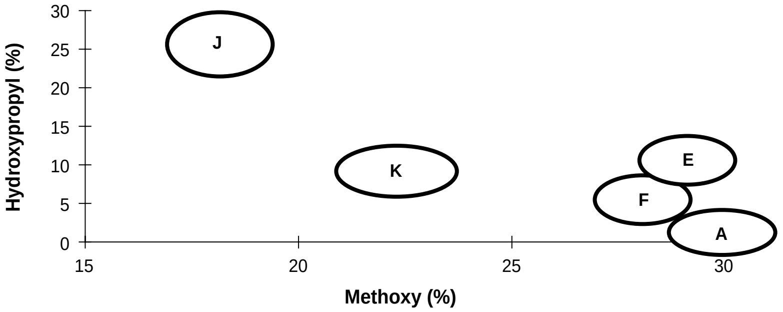


Table 1 – Typical Properties of METHOCEL Cellulose Ethers[a]

Product	MeO (%)	HPO (%)	Viscosity (mPa•s)[b]	NaCl (%)	Fe (ppm)[c]	H_2O (%)
METHOCEL K100	23.0	6.5	80 - 120	<2.0	<150	<3.0
METHOCEL F50	28.5	6.0	40 - 60	<1.5	<150	<3.0
METHOCEL E50	29.0	11.5	45 - 55	<1.5	<150	<3.0
METHOCEL 181 (E15)	29.0	10.0	13 - 18	<3.0	<150	<6.0
METHOCEL A15 LV	30.0	—	12 - 18	<2.0	<150	<3.0

[a] Properties were measured according to ASTM D2363.

[b] 2% w/w in water.

[c] METHOCEL Premium and PVC grades are <50ppm Fe.

Table 2 – Solution Properties of METHOCEL Cellulose Ethers

Product	Gel Temp. (°C)	Extractable Cellulose Ether[a] (%)	IFT[b] (dyne/cm)	Viscosity[c] (mPa•s)	Application
METHOCEL K100	72	0.42	15.6	100	Rigid PVC, low porosity, high bulk density
METHOCEL F50	67	1.58	11.2	50	General purpose suspending agent
METHOCEL E50	60	2.46	8.6	50	Flexible PVC, high porosity, low VCM residuals
METHOCEL 181 (E15)	62	3.20	7.5	15	Flexible PVC, high porosity, low VCM residuals

[a] In trichloroethylene (TCE) at 30°C.

[b] In TCE/water.

[c] 2% w/w in water.

Aqueous solutions of METHOCEL cellulose ethers reduce the interfacial tension (IFT) of the vinyl chloride monomer, facilitating dispersion and yielding smaller droplets. METHOCEL cellulose ether forms a skin at the interface, preventing droplets from coalescing. Upon heating, cellulose ethers dehydrate, forming a gel that further strengthens the protective film. The gelling temperature determines the application temperature of the cellulose ether. Cellulose ethers show a limited solubility in organic solvents. Higher grain porosities are observed with increased solubility. Table 2 lists the solution properties of METHOCEL cellulose ethers.

Interfacial tension is determined by substitution pattern, concentration of the cellulose ether, temperature, and nature of the organic phase. Some typical interfacial tension (IFT) values of 0.05% cellulose ether solutions and 1,2-dichloroethane at 30°C for different cellulose ether products are summarized in Table 3. Within the chemistry of METHOCEL cellulose ethers, IFT increases in the following order: J < E < F < A < K. The lower the IFT value, the smaller the initial droplet size. The highly substituted J chemistry products show the lowest IFT values, indicating a more hydrophobic nature. METHOCEL K products have the lowest level of substitution and show the lowest reduction of interfacial tension.

METHOCEL solutions gel when the temperature reaches a certain level. The strength of gel increases with:

- higher methoxy substitution
- lower hydroxypropyl substitution
- higher temperature
- higher concentrations
- higher molecular weight

Table 3 – IFT Values of a 0.05% Aqueous Solution of Cellulose Ethers with 1,2-Dichloroethane

METHOCEL	Interfacial Tension (dynes/cm)
K100	8.66
F50	5.17
E50	4.03
181 (E15)	4.34
A15 LV	7.36

Table 4 – Gel Temperatures of METHOCEL Cellulose Ethers

METHOCEL	Gel Temperature (°C)	Recommended Reactor Temperature (°C)
K100	70	70 - 85
F50	56	60 - 70
E50	57	60 - 70
181 (E15)	57	60 - 70
A15 LV	48	50 - 60

Table 5 – Porosity of PVC as a Function of Cellulose Ether Solubility in Trichloroethylene

METHOCEL	% of Cellulose Ether Extractable in TCE at 30°C	Porosity of PVC (mL/g)
K100	0.42	0.0632
F50	1.58	0.1054
E50	2.46	0.1863
181 (E15)	3.20	0.2236

It can be shown that gel strength has a small impact on the average grain size of PVC. Particle diameters have been found to be a direct function of interfacial tension multiplied by the 0.2 power of the gel strength of a 5% aqueous solution at 65°C. The gel strength of METHOCEL products decreases in the following order: A > F > E > K > J.

Gel temperature is also strongly determined by the substitution pattern. Different reaction temperature ranges are recommended to make full use of the gelation effect (Table 4).

Cellulose ethers are partially soluble in vinyl chloride monomer (see Table 2). The solubility in organic solvents determines grain porosity and is reciprocally proportional to the interfacial tension (Table 5).

Organosolubility decreases along with the hydrophobicity of METHOCEL cellulose ethers in the following order: J > E > F > A > K. There is strong evidence that only the low molecular weight fractions of a hydroxypropyl methylcellulose are soluble in organic solvents. The less viscous products are more soluble in the monomer and yield higher porosity. The results of METHOCEL E50 and E15 cellulose ether in Table 5 illustrate this effect.

Polymerization Process Factors

Choosing a METHOCEL Product

Vinyl chloride monomer polymerization trials have been carried out with some typical METHOCEL cellulose ethers to illustrate the effects of interfacial tension, organosolubility, and gel strength on PVC morphology (Table 6). All experiments were carried out in a 100-L laboratory reactor at a fixed temperature of 57.5°C. METHOCEL cellulose ethers were the sole suspending agent and were added at a level of 0.2%.

Grain size differences can be explained by variations in interfacial tension. METHOCEL K100 has the highest IFT value, resulting in larger initial monomer droplets and eventually causing larger resin grains. Gel strength affects properties only by the power of 0.2, and its effect is probably hidden by other effects within this series of experiments.

Bulk density and grain porosity are directly related to interfacial tension. High IFT values, such as in the case of METHOCEL K100, result in high bulk densities and extremely low porosities. The opposite is observed for METHOCEL E50. METHOCEL 181 (E15) has been developed to further improve resin porosity.

Determining the Level of METHOCEL Products

The quantity of METHOCEL required for maximum performance is a function of equipment size, degree of agitation, the chemical make-up of the polymerization system, and the particle size range desired. The amount required for large-scale operations will generally range between 0.05 and 0.10% of the monomer weight. Table 7 lists suggested levels for various size reactors. Experience has shown that small equipment requires more protective colloid and that the values in the table have to be adjusted to suit specific equipment layouts and polymerization charges.

Table 6 – PVC Resin Properties Using METHOCEL Suspending Agents

METHOCEL	Particle Diameter (μm)	Bulk Density (g/mL)	Grain Porosity (mL/g)
K100	150	0.72	0.02
F50	124	0.56	0.15
E50	124	0.52	0.21
181 (E15)	118	0.55	0.22

Table 7 – Percent METHOCEL Cellulose Ether for Reactors

Size of Reactor	Speed of Agitator	% METHOCEL[1]
1/2 gallon reactor (2 L)	150 - 170 rpm	0.2 - 0.3
1 - 2 gallon reactor (4-7 L)	150 - 170 rpm	0.2 - 0.3
20 gallon reactor (75 L)	150 - 170 rpm	0.15 - 0.18
50 gallon reactor (200 L)	150 rpm	0.08
500 gallon reactor (2000 L)	120 rpm	0.06
3000 gallon reactor (10,000 L)	120 rpm	0.05

[1] Based on monomer

Table 8 – PVC Grain Size Averages, Std. Deviation, Bulk Density and Porosity as a Function of Cellulose Ether Concentration

Concentration of Cellulose Ether (%)	Particle Mean Diameter (μm)	Standard Deviation (μm)	Bulk Density (g/mL)	Porosity (mL/g)
METHOCEL F50, Polymerization Temperature: 55°C				
0.05	367	85	0.55	0.2324
0.09	326	84	0.60	0.1670
0.12	248	89	0.63	–
0.20	154	91	0.64	0.1054
METHOCEL K100, Polymerization Temperature: 65°C				
0.05	334	120	0.56	0.1261
0.07	279	100	0.59	0.0615
0.10	261	92	–	–
0.20	217	98	0.57	0.0632

A common way to control PVC grain size is to change the amount of cellulose ether added to the reactor (Table 8). Increasing the concentration of the METHOCEL suspending agent results in better surface coverage of the initial monomer droplets and reduces the aggregation tendency during the "sticky" state of polymerization. Smaller particles will be obtained (see trial results of a 2-L reactor in Table 8).

Although the difference is not very large, the standard variation data of Table 8 indicate that METHOCEL F50 produces a smaller particle size distribution than METHOCEL K100.

Experience has shown that distribution of resin particle size is even smaller with METHOCEL E50. Thus, one might conclude that the lower the interfacial tension, the narrower the grain size distribution of the PVC.

The bulk density increases with an increase in METHOCEL F50 concentration while the corresponding porosity decreases. The trend with METHOCEL K100 is less clear concerning bulk density, which remains rather constant with variation of the concentration of the suspending agent.

Order of Addition

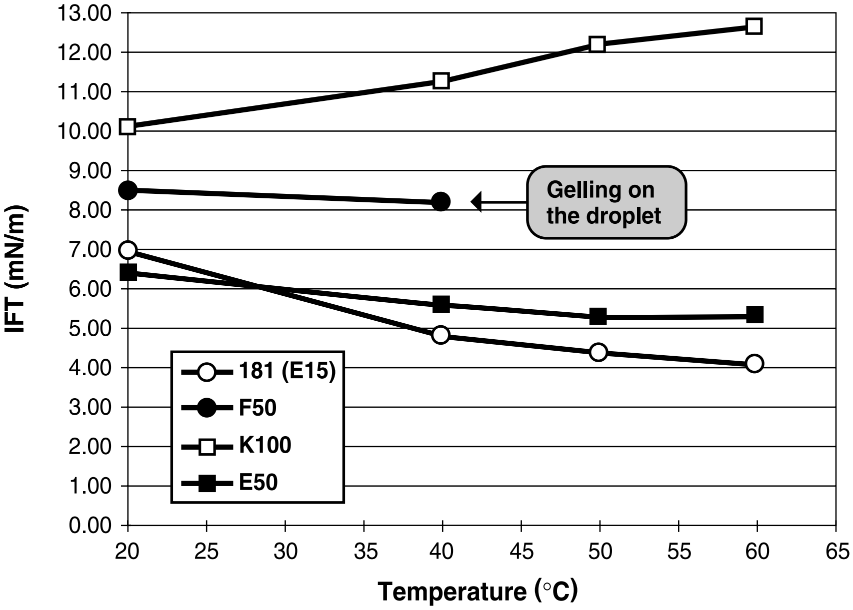
The best control of particle size is obtained by charging (loading) the water and solution of METHOCEL into the reactor prior to adding the monomer. There are several practical reasons for doing so:

- when monomer is added first, subsequent addition and mixing of the solution of METHOCEL becomes difficult because of high vapor pressures built up by the monomer
- pre-wetting of the reactor wall with water lessens the build-up of resin on scratches, etc.
- adding monomer prior to addition of the water and METHOCEL can result in a high percentage of coarse particles.

Temperature Effects

Hydroxypropyl methylcellulose dehydrates in aqueous solution when the temperature rises, forming a gel that contributes to droplet protection against coalescence. This gelling effect is reversible when the temperature is reduced below the gel point. When using METHOCEL cellulose ethers as suspending agents, one must consider that the surface activity of these products decreases when the products are heated above the gel point.

Figure 3 – Interfacial Tensions of 0.05% Aqueous Hydroxypropyl Methylcellulose Solutions TCE Systems as a Function of Temperature Measured with a Drop/Volume Tensiometer



Hot-water reactor-charging techniques are often used to reduce the batch time of vinyl chloride monomer polymerization. If METHOCEL cellulose ethers are present as suspending agents, it is important that the protective droplet film be formed at temperatures below the gel point before hot water or steam is added to the reactor. It is recommended that METHOCEL suspending agents be added to only part of the aqueous phase at a temperature 20° below the gel temperatures indicated in Table 4 and that an equilibrium with the vinyl chloride monomer phase be reached while stirring. The remaining water quantity can be added at higher temperatures. Figure 3 illustrates the changes in interfacial tension of METHOCEL products with temperature.

The interfacial tension first decreases with the increase in temperature with the exception of METHOCEL K100. The curves end where the cellulose ether starts to gel at the TCE droplet surface. The strengths or the yield values of these gels are highly dependent on type or degree of substitution and molecular weight. METHOCEL cellulose ethers with high gel strengths (i.e., F chemistry) show a fast response to the increase in temperature. At a temperature of about 20°C below the gel point, measured in homogenous solution, the cellulose ether starts to gel at the TCE droplet surface as a result of increased local concentration, and it gives excellent droplet protection. METHOCEL K and E products have lower gel strength and show a less distinct gelling effect. Although their ability to give a strong protective film on the droplet surface is less pronounced, they perform within a broader temperature range.

Product Purity and Form

METHOCEL premium products are available for applications where high purity is important. Premium grades of METHOCEL cellulose ethers should also be considered when the PVC resin requires optimum electrical properties. For PVC resins used in food-packaging applications, all standard grades of METHOCEL products can be used as indirect food additives, meeting the requirements of FDA and EC legislation.

Most METHOCEL products are available as powders. To improve product handling, dust formation, flowability, and cold water dispersibility, Dow offers some grades of METHOCEL cellulose ethers with larger grain size. Table 9 gives an overview of all available METHOCEL products suitable as suspending agents for vinyl chloride monomer polymerization.

Table 9 – Availability List of METHOCEL Products

METHOCEL	Powder Form	Non-dust Form
K100	✓	
F50	✓	✓
E50	✓	✓
181 (E15)		✓
A15 LV	✓	

Using METHOCEL Cellulose Ethers with Other Suspending Agents

Although the use of METHOCEL suspension agents alone for vinyl chloride monomer polymerization allows the production of many PVC resin grades of various grain sizes, porosities, and morphologies, PVC producers often prefer combinations of several suspending agents to optimize their resin properties. Combinations with polyvinyl alcohols yield recipes with excellent grain size control over a wide range of shear profiles. METHOCEL cellulose ethers can be successfully combined with secondary suspending agents such as hydroxypropyl cellulose or polyvinyl alcohols with low hydrolysis levels to increase grain porosity.

Preparation of Solutions of METHOCEL Cellulose Ethers

Solubilization Techniques

Because very low levels of METHOCEL are used in the reactor charge, very small differences in concentration can affect particle size distribution. To minimize such variances, it is generally best to weigh the METHOCEL product into the reactor in the form of a stock solution. A thorough study of Dow literature covering preparation of solutions with METHOCEL is recommended. Several techniques are available depending upon the process used in a specific PVC plant. It is also suggested that operating procedures include instructions for measuring and recording the final temperature of the solution of METHOCEL to ensure that dissolution is complete.

Equipment for Dissolution of METHOCEL Cellulose Ethers

To ensure product purity, noncorrosive materials or coatings should be used in equipment for preparing solutions of METHOCEL products. Materials such as 304 stainless steel, nickel, and glass linings have proved acceptable in service. Six horsepower per 1000 gallons of solution should prove ample for dissolving powdered METHOCEL products.

A system used successfully at The Dow Chemical Company begins with preparation of the solution of METHOCEL in a glass-lined jacketed 3,500 gallon Pfaudler kettle with standard agitation at 80 to 90 rpm. Half of the required amount of deionized water at 85°C (185°F) is metered into the Pfaudler kettle. METHOCEL product is then added, and agitation is continued for 45 minutes, at which time the balance of the water is added.

Cooling water is circulated in the jacket until the temperature is cold enough to obtain complete solubility of the METHOCEL. The different METHOCEL product types require different cooling temperatures for solubilization:

- "A" products down to 5 to 10°C (41 to 50°F)
- "E" products down to 20°C (68°F)
- "F" and "K" products down to 25°C (77°F)

At the loading stations, the required amount of solution of METHOCEL is weighed into a nickel drum and drawn into the reactors by vacuum.

Quality Control

Because the quantity of METHOCEL cellulose ethers used in PVC polymerization reactions is measured in parts per million, good control of the quantity added to the reactor is a necessity. The procedure for preparing the solution of the METHOCEL products must be carefully standardized. Final temperature of the solution should be recorded to assure reproducibility of results. The concentration of the finished solution should be checked either by gravimetric evaporation or colorimetric tests (phenol, sulfuric acid). Demineralized water or its equivalent should be used both for polymerization and for preparing solutions of METHOCEL products.

Technical Literature

Control of PVC resin morphology produced by suspension polymerization of vinyl chloride has been the subject of a vast number of technical papers. The detailed understanding of the role of the suspending agent on the bulk properties of PVC is of paramount importance to the manufacturer to meet the current needs of the market and to be able to face future challenges. The following list of technical papers provides insight into the mechanism of cellulose ethers as suspending agents in PVC production.

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Printed in U.S.A.
Published March 1999

Form No. 192-01188-399AMS US
192-01197-399AMS A4