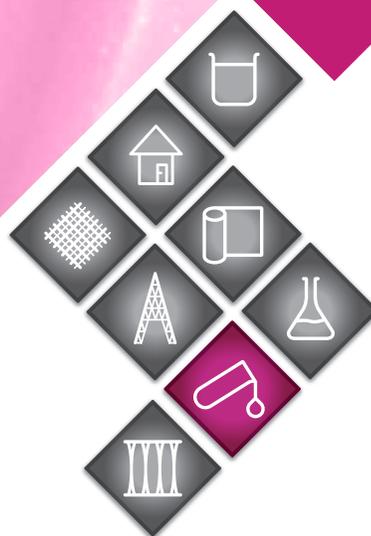


SEKISUI

POLYVINYL  
ALCOHOL  
IN EMULSION  
POLYMERIZATION



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## About the Company

The Sekisui Chemical Group is a global company that operates in three major businesses: High Performance Plastics, Urban Infrastructure and Environmental Products, and Housing. Founded in 1947 and currently headquartered in Osaka and Tokyo, Japan, Sekisui strives to deliver a wide range of products and services to enrich people's lives and the social infrastructure.



Architectural Glass



Urban Infrastructure and Environmental Product

## Our Promise

Through prominence in technology and quality, Sekisui Chemical Group will contribute to improving the lives of the people of the world and the Earth's environment, by continuing to open up new frontiers in residential and social infrastructure creation and chemical solutions.



Housing

## Sekisui Specialty Chemicals

Sekisui produces and sells one of the most complete lines of polyvinyl alcohol in the world. Since the introduction of Selvol Polyvinyl Alcohol, we have developed a high level of expertise in both the production and use of PVOH.

Based in Dallas, Texas, Sekisui Specialty Chemicals is a leading polyvinyl alcohol supplier with manufacturing facilities in Calvert City, Kentucky, Pasadena, Texas and Tarragona, Spain. The combined capacity of the three plants makes Sekisui a leading global merchant supplier of polyvinyl alcohol.

Sekisui's commitment to polyvinyl alcohol is especially evident in our research and applications support activities. We have one of the largest technical services, product application, and analytical services groups in the world. Research and application development is carried out at our facilities in Houston, Texas. Sekisui also has a global sales force located in offices worldwide to respond more quickly to the needs of our customers.



## Introduction

This brochure reviews polyvinyl alcohol as a protective colloid for the emulsion polymerization of polyvinyl acetate. For more detailed information on specific applications, the preparation of polyvinyl alcohol solutions, please refer to our other brochures, visit our website at [www.selvol.com](http://www.selvol.com), or call our Product Information Center at +1-281-280-3460.



## Environmental, Health, and Safety

Please refer to our Material Safety Data Sheets (MSDSs) or Safety Data Sheets (SDSs) for information on the safe use and handling of Selvol Polyvinyl Alcohol, including toxicity, fire, and explosion hazards, as well as environmental effects. An MSDS can be obtained online at [www.selvol.com](http://www.selvol.com).

## FDA Compliance

Polyvinyl alcohol is used in many food contact applications, including food packaging adhesives and coatings for paper and paperboard. For more specific information on the FDA status of any of our grades, please contact our Product Information Center at +1-281-280-3460.

TABLE 1:  
Selvol Polyvinyl Alcohol Right-to-Know Information

Ingredient	CAS Number
Selvol Polyvinyl Alcohol	
▪ Super and Fully Hydrolyzed	9002-89-5
▪ Partially and Intermediate Hydrolyzed	25213-24-5
Water	7732-18-5
Methanol	67-56-1
Sodium Acetate	127-09-3

## Selvol Polyvinyl Alcohol

Selvol Polyvinyl Alcohol is a white, granular, water-soluble resin manufactured by polymerizing vinyl acetate and hydrolyzing the resultant polymer to produce the alcohol (Figure 1).

Because PVOH is synthesized from polyvinyl acetate, a variety of different grades of Selvol Polyvinyl Alcohol is available that varies in molecular weight and hydrolysis level. These two factors are the major determinants of the performance properties of PVOH.

FIGURE 1:  
General Structure of Polyvinyl Alcohol

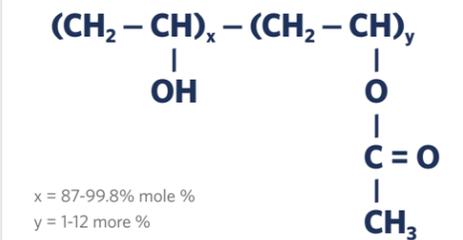


TABLE 2:  
Selvol Polyvinyl Alcohol Molecular Weight

Viscosity <sup>1</sup> (cP)	Viscosity Type	Degree of Polymerization	Average Weight Molecular Weight Range	Number Average Molecular Weight Range
3-6	Low	150 - 650	13,000 - 50,000	7,000 - 23,000
22-30	Medium	1000 - 1500	85,000 - 124,000	44,000 - 65,000
45-72	High	1600 - 2200	146,000 - 186,000	70,000 - 101,000

<sup>1</sup> 4% aqueous solution viscosity.

Molecular weight is a measure of polymer chain length and is typically reported as a 4% aqueous solution viscosity (Table 2).



Molecular Structure PVOH

TABLE 3:  
Description of the Different Hydrolysis Levels for PVOH

Grade	Hydrolysis Mole %
Super	99.3+
Fully	98.0-98.8
Intermediate	90.0-97.0
Partially	87.0-89.0

Hydrolysis level is a measure of the mole % hydroxyl functionality on the polymer. The hydrolysis level of PVOH is typically categorized as shown in Table 3.

# Selvol Polyvinyl Alcohol General Properties

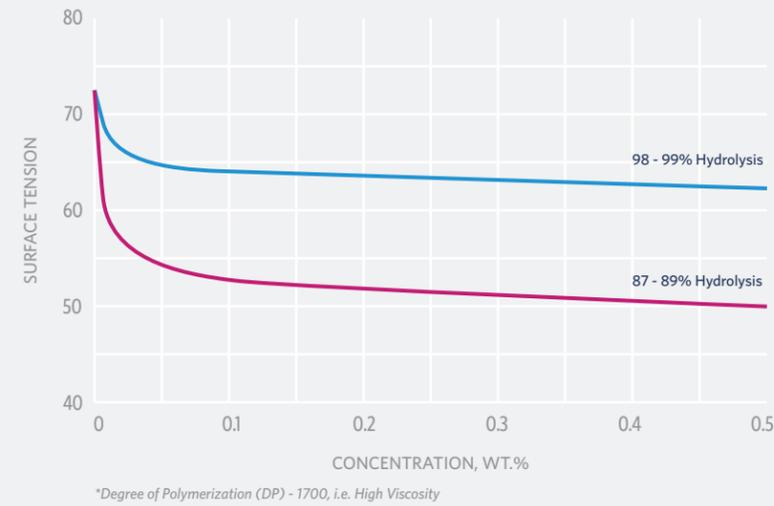
## SOLUBILITY

All Selvol PVOH grades are readily soluble in water. Other solvents include dimethyl sulphoxide, acetamide, glycols, and dimethyl formamide. The conditions for dissolution of PVOH in water are primarily governed by the degree of hydrolysis, but they are also influenced by molecular weight, particle size distribution, and crystallinity.

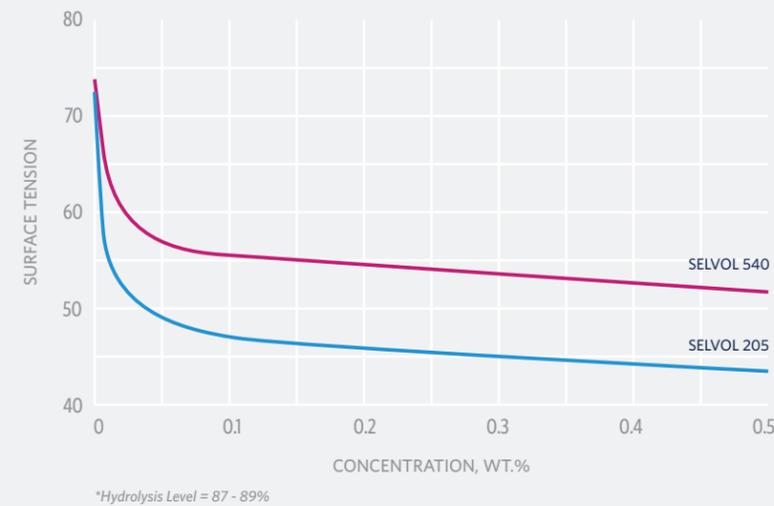
Optimum solubility occurs with PVOH grades that have a hydrolysis level between 87-89%. Grades in this range are highly soluble in cold water. However, for total dissolution, it is recommended that, after the PVOH is added to the water, it must be heated to 185-190 °F and held at this temperature for 30 minutes. Higher hydrolysis grades require higher temperatures (200-205 °F) because of the increased hydrogen bonding associated with its lower acetate levels. Please refer to our Selvol Polyvinyl Alcohol Solution Preparation Guidelines for additional information.



**FIGURE 2:**  
Effect of Hydrolysis Level on the Surface Tension of Aqueous PVOH Solutions



**FIGURE 3:**  
Effect of Hydrolysis Level on the Surface Tension of Aqueous PVOH Solutions



## SURFACE TENSION

Because PVOH contains both hydrophilic hydroxyl groups and hydrophobic acetate groups, these compounds have some surface activity. This results in aqueous PVOH solutions having surface tension values lower than those of pure water. The surface tension of PVOH solutions varies with concentration, temperature, degree of hydrolysis, and molecular weight. In general, the lower the hydrolysis level, the lower the surface tension of the aqueous solution, as shown in Figure 2. Surface tension also varies when comparing grades of equal hydrolysis level but different molecular weight (Figure 3). In this case, materials of lower molecular weight have slightly lower surface tension values.

## FOAMING

Aqueous solutions of PVOH, because of their low surface tension, have a tendency to foam. Foaming is dependent on the level of hydrolysis, as well as the mechanical dynamics unique to each preparation and end use. Partially hydrolyzed grades of PVOH are more susceptible to foaming than solutions of PVOH with higher degrees of hydrolysis. In order to minimize foaming, the following suggestions should be followed:

1. Agitation should be sufficient to move the water surface without whipping air into the system
2. PVOH solutions should not be boiled.
3. Recirculation and/or feed lines should not be placed so they introduce air into the system.

In addition to following the above guidelines, it may also be necessary to add defoamers to the PVOH solution. Table 4 lists several recommended defoamers for use with PVOH solutions. The advantage of Selvol 800 grades is that little or no additional defoamer may be required.

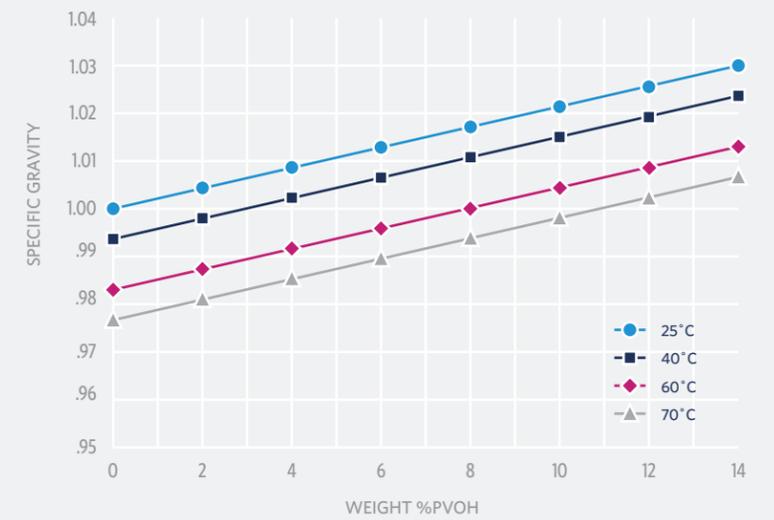
## PRESERVATION

If PVOH solutions are stored for longer than 24 hours before use, it is recommended that a biocide be added to prevent biocontamination. See Table 5 for recommended biocides.

## SPECIFIC GRAVITY

The specific gravity of PVOH solutions depends on concentration and temperature, but is independent of PVOH grade. Figure 4 shows the specific gravity as a function of concentration at various temperatures.

**FIGURE 4:**  
Specific Gravity of Selvol PVOH Solutions as a Function of Concentration at Various Temperatures



**TABLE 4:**  
Recommended Defoamers for Selvol Polyvinyl Alcohol\*

Defoamer	Supplier	Use Level
FC 407	ESP Enterprises	<1%, d/d
Antifoam 116	Harcros	< 1%, d/d
Industrol DF 132	BASF	< 1%, d/d

\* Note: The FDA compliance status of the recommended additives should be verified with the respective manufacturer.

**TABLE 5:**  
Recommended Biocides for Use with PVOH Solutions\*

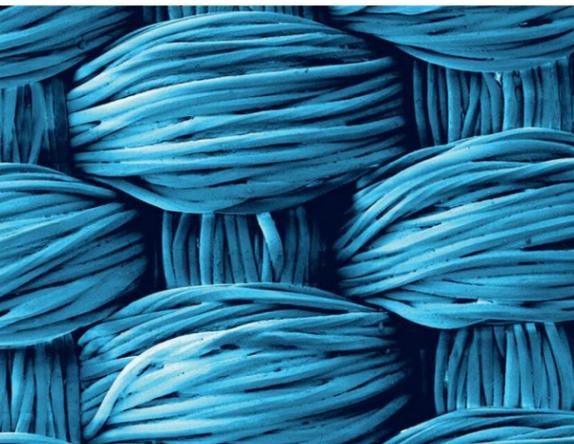
Biocide	Supplier	Use Level
Kathon LX	Dow Chemical	< 50 ppm
Dowicil 75	Dow Chemical	1000 - 2000 ppm

\* Note: The FDA compliance status of the recommended additives should be verified with the respective manufacturer.



## Polyvinyl Alcohol Business

Sekisui's Selvol Polyvinyl Alcohol (PVOH) is an excellent emulsifying and dispersing agent for a wide variety of materials. In particular, it is one of the most widely used polymers for the colloidal stabilization of vinyl-acetate-based emulsions (Table 6). Polyvinyl acetate (PVAc) homopolymer and copolymer emulsions prepared in the presence of PVOH have a number of different applications including adhesives, paints, and textile finishes. Of these, the largest use of PVOH as a colloidal stabilizer is in the production of vinyl-acetate-based emulsions for adhesives.



Polymers prepared for the adhesives market employ PVOH because it adds a variety of beneficial properties to the final product.

These properties include:

1. Improved adhesion to hydrophilic substrates.
2. Good machinability.
3. Easy clean-up.
4. Good wet tack.
5. Rapid setting speed.
6. Good heat resistance.
7. Low degree of blocking.
8. High thickening response.
9. Crosslinkability.

In addition to vinyl acetate, PVOH is also used as a stabilizer for the suspension polymerization of vinyl chloride and the dispersion polymerization of styrene.

TABLE 6:

STANDARD GRADES							
Grade	Hydrolysis, %	Viscosity, cP <sup>1</sup>	pH <sup>2</sup>	Volatiles, % Max		Ash, % Max <sup>5</sup>	Methanol, wt % Max
				Total <sup>3</sup>	VOC <sup>4</sup>		
<b>Fully Hydrolyzed</b>							
Selvol PVOH 103/E 103	98.0-98.8	3.5-4.5	5.0-7.0	5.0	1.0	1.2	0.9
Selvol PVOH 107/E 107	98.0-98.8	5.5-6.6	5.0-7.0	5.0	1.0	1.2	0.9
Selvol PVOH 310/E 310	98.0-98.8	9.0-11.0	5.0-7.0	5.0	1.0	1.2	0.9
Selvol PVOH 325/E 325	98.0-98.8	28.0-32.0	5.0-7.0	5.0	1.0	1.2	0.9
Selvol PVOH 325LA**	98.0-98.8	28.5-31.5	5.0-7.0	5.0	1.0	0.6	0.9
Selvol PVOH 350	98.0-98.8	62.0-72.0	5.0-7.0	5.0	1.0	1.2	0.9
<b>Intermediate Hydrolyzed</b>							
Selvol PVOH 418	91.0-93.0	14.5-19.5	4.5-7.0	5.0	1.0	0.9	0.9
Selvol PVOH 425	95.5-96.5	27.0-31.0	4.5-6.5	5.0	1.0	0.9	0.9
Selvol PVOH 443	92.0-94.0	53.0-63.0	4.5-6.5	5.0	1.0	0.9	0.9
<b>Partially Hydrolyzed</b>							
Selvol PVOH 502	87.0-89.0	3.0-3.7	4.5-6.5	5.0	1.0	0.9	0.9
Selvol PVOH 203/E 203	87.0-89.0	3.5-4.5	4.5-6.5	5.0	1.0	0.9	0.9
Selvol PVOH 504	87.0-89.0	4.0-5.0	4.5-6.5	5.0	1.0	0.7	0.9
Selvol PVOH E 4/88LA*	87.0-89.0	4.0-5.0	4.5-6.5	5.0	1.0	0.9	0.9
Selvol PVOH E 5/88LA*	87.0-89.0	5.0-6.0	4.5-6.5	5.0	1.0	0.7	0.9
Selvol PVOH 205/E 205	87.0-89.0	5.2-6.2	4.5-6.5	5.0	1.0	0.7	0.9
Selvol PVOH E 8/88	87.0-89.0	7.0-9.0	4.5-6.5	5.0	1.0	0.7	0.9
Selvol PVOH 508	87.0-89.0	7.5-9.5	4.5-6.6	5.0	1.0	0.7	0.9
Selvol PVOH 513	87.0-89.0	13.0-15.0	4.5-6.5	5.0	1.0	0.7	0.9
Selvol PVOH 518	87.0-89.0	17.5-20.5	4.5-6.5	5.0	1.0	0.7	0.9
Selvol PVOH 523/E 523	87.0-89.0	23.0-27.0	4.5-6.5	5.0	1.0	0.5	0.9
Selvol PVOH 540	87.0-89.0	45.0-55.0	4.5-6.5	5.0	1.0	0.5	0.9
<b>SPECIALTY GRADES</b>							
Grade	Hydrolysis, %	Viscosity, cP <sup>1</sup>	pH <sup>2</sup>	Volatiles, % Max		Ash, % Max <sup>5</sup>	Methanol, wt % Max
				Total <sup>3</sup>	VOC <sup>4</sup>		
<b>Polymerization</b>							
Selvol PVOH 805	87.0-89.0	5.20-6.20	4.5-6.5	5.0	1.0	0.7	0.9
Selvol PVOH 818	87.0-89.0	17.0-21.0	4.0-6.5	5.0	1.0	0.3-0.6	0.9
Selvol PVOH 823	87.0-89.0	23.0-27.0	4.5-6.5	5.0	1.0	0.5	0.9
Selvol PVOH 830	87.0-89.0	29.0-35.0	4.5-6.5	5.0	1.0	0.5	0.9
Selvol PVOH 840	87.0-89.0	45.0-55.0	4.5-6.5	5.0	1.0	0.5	0.9

\* Low Ammonia (for E grades)  
\*\* Low Ash.

<sup>1</sup> 4% aqueous solution, 20°C.  
<sup>2</sup> 4% aqueous solution.

<sup>3</sup> Total volatiles incl. water.

<sup>4</sup> Volatile organic compound, primarily methanol. (max 0.9%) with methyl acetate.

<sup>5</sup> As % Na<sub>2</sub>O, corrected volatiles.

<sup>6</sup> 10% aqueous solution, 25°C.

<sup>7</sup> 10% aqueous solution.

<sup>8</sup> Use of Selvol PVOH 2035 is covered by U.S. Patent No. 5,057,570.

## Selvol Polyvinyl Alcohol as a Protective Colloid

Choice of the Appropriate Grade of Selvol Polyvinyl Alcohol In choosing the appropriate grade of PVOH to use as the protective colloid, one must consider the composition of the emulsion to be produced, polymerization conditions, and the desired properties of the end product. In addition to the process conditions and the composition of the emulsion produced, the final emulsion properties are largely dictated by the molecular weight and hydrolysis level of the PVOH.

The upper portion of Figure 5 shows emulsion properties as a function of molecular weight at a constant hydrolysis level; the effect of hydrolysis at constant molecular weight is given in the lower portion of the table. In general, higher molecular weight PVOH grades result in emulsion polymers with higher viscosities, increased shear thinning, higher tensile strength, and higher wet tack.

Lower hydrolysis levels contribute to good stability, increased water sensitivity, increased thixotropy, and improved freeze-thaw stability.

## General Recipe and Procedure

Emulsion polymerization, using PVOH as the protective colloid, can be performed using either batch or continuous processes. The quantity of polyvinyl alcohol used in emulsion polymerization is between 4-10 weight % based on the vinyl acetate monomer (VAM). Table 5 displays the emulsion properties associated with different grades of PVOH. These comparisons were made on emulsions produced using the general recipe and procedure shown in 70-74 °C Table 7 and Figure 6.

FIGURE 5: Emulsion Properties as a Function of PVOH Molecular Weight and Hydrolysis Level



FIGURE 6: Polymerization Procedure

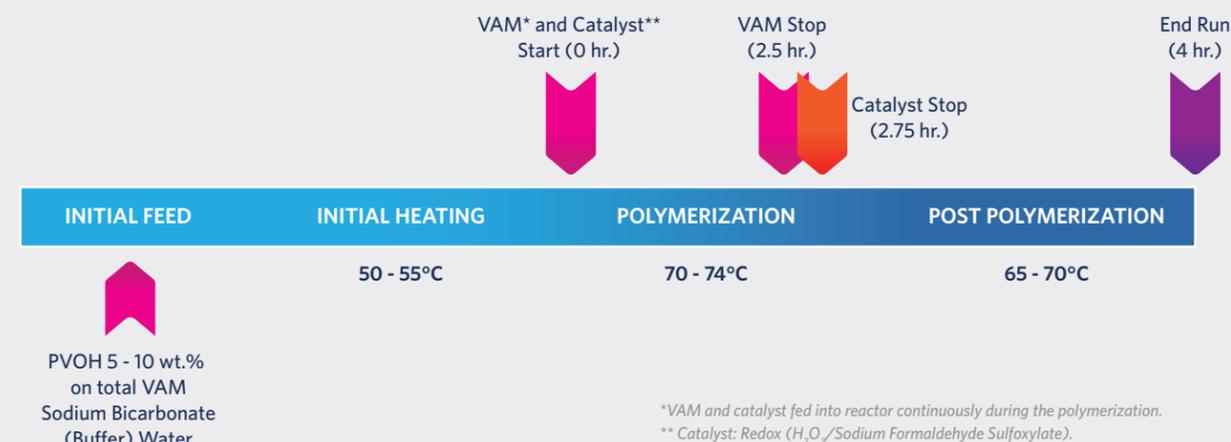
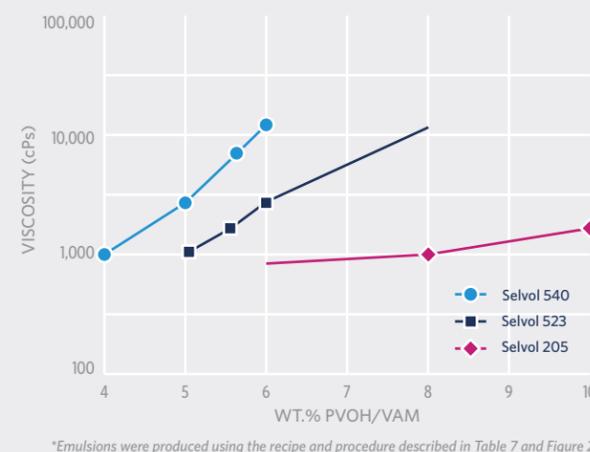


FIGURE 7: Effect of PVOH Content and Molecular Weight on the Emulsion Viscosity



## Effect of PVOH Molecular Weight on Emulsion Properties

The molecular weight of the PVOH used as a protective colloid in emulsion polymerization can influence the properties of the emulsion (Table 6). The properties most influenced by the PVOH molecular weight are the emulsion viscosity and rheological behavior. The relationship between final emulsion viscosity and the molecular weight of the PVOH is exponential, as illustrated in Figure 6. At a 6% weight ratio of PVOH to vinyl acetate monomer (% PVOH/VAM), the viscosity increases from 690 cP for an emulsion produced with Selvol Polyvinyl Alcohol 205 to 2845 cP for an emulsion produced with Selvol Polyvinyl Alcohol 523. The change in viscosity is even more pronounced when Selvol Polyvinyl Alcohol 540 is used as the protective colloid. Figure 7 also shows the relationship between the final emulsion viscosity and the % PVOH/VAM. As the % PVOH/VAM is increased, the emulsion viscosity also increases. Higher molecular weight grades of PVOH, such as Selvol Polyvinyl Alcohols 540 and 523, are more effective at raising the emulsion viscosity, with small changes in the % PVOH/VAM, than are low molecular weight grades of PVOH.

Emulsion polymers produced using PVOH as the protective colloid all exhibit shear thinning behavior. The degree to which the emulsion is shear thinning is dependent on the molecular weight of the PVOH. When higher molecular weight grades of PVOH are used, the emulsion generally exhibits more shear thinning and has a higher viscosity at a similar shear rate than does an emulsion produced with a lower molecular weight grade of PVOH (Figure 8). In addition to being more shear thinning, emulsions produced using high molecular weight grades of PVOH are also more thixotropic. These trends result from more inter-polymer chain entanglement associated with using a high molecular weight grade of PVOH (visually depicted in Figure 9).

FIGURE 8: Emulsion Viscosity vs. Shear as a Function of PVOH Molecular Weight

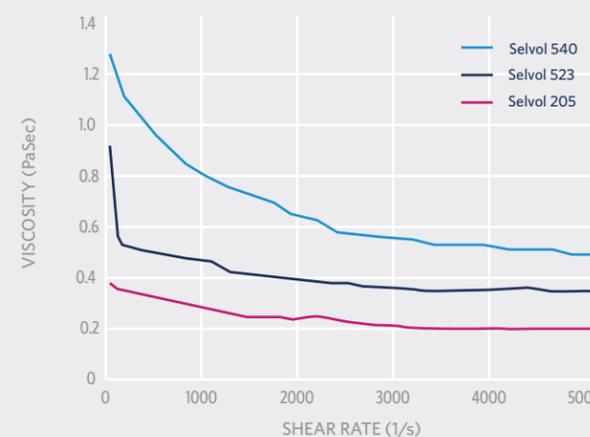


TABLE 6: Typical Properties of Emulsions Prepared Using Selvol Polyvinyl Alcohol

Selvol PVOH Grade	wt.% PVOH/VAM	Viscosity (cP)	pH	Accel. Sed. <sup>2</sup> (%)	% Free Monomer
205	6	690	4.9	<1	0.58
805	6	860	4.9	<1	0.50
418	6	1010	5.2	<1	0.60
523	5	1160	5.0	<1	0.31
823	5	1100	4.9	<1	0.42
540	5	2965	5.0	<1	0.62
840	5	2790	5.2	<1	0.56

<sup>2</sup> Accelerated sedimentation values were obtained by diluting a 55% solids emulsions to 25% solids and centrifuging the resultant dispersion for 10 minutes at 2800 rpm.

TABLE 7: General Emulsion Recipe

Process Type	Semi Batch
Targeted % Solids	55%
Ratio of PVOH to VAM *	5 - 10%
Initiation System	Redox
Initial VAM Charge	1/8 of total VAM
Initiation Temperature	50 - 55 °C
Polymerization Temperature	70 - 74 °C

\* Based on weight

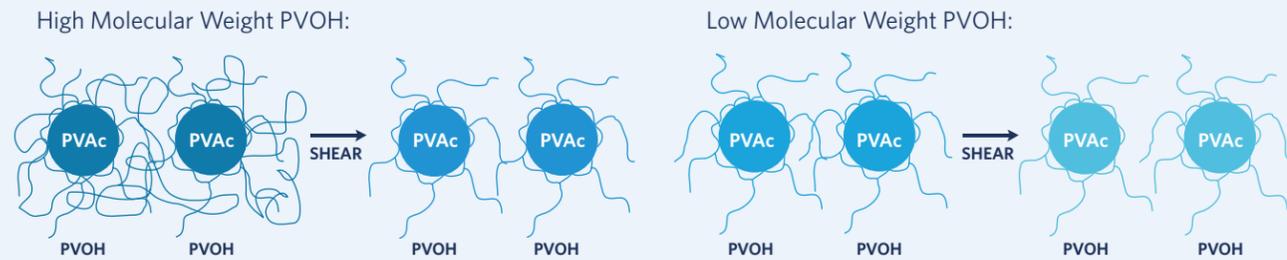


FIGURE 9: Higher Molecular Weight Grades of PVOH Can Have More Inter-Polymer Chain Entanglement Which Leads to Increased Shear Thinning Behavior

TABLE 8: Emulsion Properties as a Function of PVOH Hydrolysis Level<sup>1</sup>

% Hydrolysis	PVOH/VAM	% Accel. Sed. <sup>2</sup>	D <sub>n</sub> <sup>3</sup>	D <sub>w</sub>	D <sub>n</sub> /D <sub>w</sub>
88	5	< 1	0.708	< 1	1.27
92	5	> 6	NA	< 1	NA
88	6	< 1	0.729	< 1	1.22
92	6	< 1	0.801	< 1	1.21

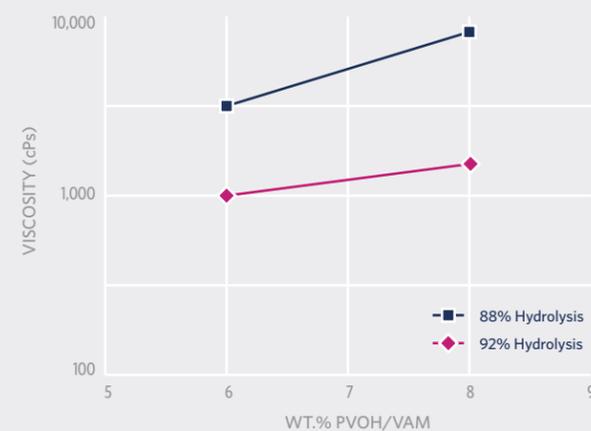
<sup>1</sup> Emulsions were prepared using the recipe and procedure described in Table 7 and Figure 6.  
<sup>2</sup> Accelerated sedimentation values were obtained by diluting a 55% solids emulsions to 25% solids and centrifuging the resultant dispersion form 10 minutes at 2800 rpm.  
<sup>3</sup> Particle size was measured using a Brookhaven Disk Centrifuge particle size analyzer model BI-DCP.

Effect of Selvol Polyvinyl Alcohol PVOH Hydrolysis Level on Emulsion Properties The degree of hydrolysis of the PVOH, when used as a protective colloid to produce an emulsion, affects the emulsion stability, particle size, viscosity, and rheology, as well as the properties of the dry polymer film. Partially hydrolyzed grades of PVOH (87.0-89.0%) are generally favored for producing vinyl-acetate-based emulsions because of the good emulsion stability associated with these grades. However, emulsions produced with partially hydrolyzed grades of PVOH as the protective colloid also exhibit a high degree of water sensitivity. For certain applications, it may be necessary to have a polymer that is more water-resistant. Blends of PVOH grades that differ in hydrolysis level, or an intermediate hydrolysis level grade of PVOH, can be used to obtain the proper balance of emulsion stability and water resistance of the dry emulsion film.

Emulsions produced using partially hydrolyzed grades of PVOH have a smaller particle size and are more stable than emulsions prepared with higher hydrolysis grades of PVOH. Table 8 shows the general properties of emulsions produced using similar molecular weight grades of PVOH that differ only in hydrolysis using the polymerization recipe in this brochure. In particular, at a 5 weight % PVOH/VAM, the accelerated sedimentation is higher for the emulsion produced with the 92% hydrolyzed PVOH (>6%), as compared to less than 1% for the emulsion produced with the 88% hydrolyzed PVOH. The instability of emulsions produced with 92% hydrolyzed PVOH can be overcome by increasing the %PVOH/VAM used or by adjusting the reaction conditions. Using 6 weight % PVOH/VAM, one can produce a stable emulsion with a 92% hydrolyzed PVOH.

Emulsions produced using similar molecular weight grades of PVOH, but differing in hydrolysis, exhibit different viscosity, and rheological behavior. Emulsions produced using higher hydrolysis grades of PVOH as the protective colloids are generally lower in viscosity. Figure 10 illustrates the decrease in emulsion viscosity as a function of PVOH hydrolysis level; comparing a 92% hydrolyzed PVOH to an 88% hydrolyzed PVOH. The rheology of these emulsions is also very different. Emulsions produced using higher hydrolysis grades of PVOH are more Newtonian in their flow characteristics than emulsions produced with lower hydrolysis grades of PVOH. This is illustrated in Figure 11 by the smaller thixotropy loop exhibited by the emulsion produced with a 92% hydrolyzed PVOH, as compared to the emulsion produced with an 88% hydrolyzed PVOH.

FIGURE 10: Effect of Hydrolysis Level on Emulsion Viscosity at 55% Solids (PVOH Degree of Polymerization ffi 1200, i.e. Medium Viscosity)



## Selvol PVOH 418

The 92% hydrolyzed grade of Selvol Polyvinyl Alcohol 418 can be used to produce stable emulsions exhibiting property enhancements usually associated with a higher hydrolysis grade of PVOH. These enhancements include improved compatibility with post-added fully hydrolyzed grades of PVOH when compounding adhesive formulations; higher wet tack, faster speeds of set, and improved water resistance of the dry emulsion film. Employing Selvol PVOH 418 as a protective colloid is preferred to blending PVOH grades of differing hydrolysis levels. This is recommended because it simplifies the polymerization procedure and eliminates a potential source of emulsion variability.

Using Selvol PVOH 418 as the protective colloid can improve the compounding latitude of the emulsion polymer. Figure 12 compares the compatibility of emulsions produced using either Selvol Polyvinyl Alcohols 418 or 523 as the protective colloid with post-added PVOH. The % separation was obtained by mixing equal volume percentages of a 55% solids emulsion and a 10% solids PVOH solution. This mixture is next diluted to 1000 cP viscosity and stored at 70 °C for one week; the percent separation is then measured. The results indicate that emulsions produced with Selvol PVOH 418 have complete compatibility with post-added partially and intermediate hydrolyzed grades of PVOH. The compatibility with fully hydrolyzed grades is improved for emulsions produced with Selvol PVOH 418 (92% hydrolyzed) as the protective colloid when compared to emulsions produced with Selvol PVOH 523 (88% hydrolyzed) as the protective colloid. Emulsions produced with 88% hydrolyzed grades of PVOH, such as Selvol PVOH 523, are only compatible with post-added PVOH grades of the same hydrolysis level.

In addition to the improvements in compounding, an emulsion produced with Selvol PVOH 418 exhibits improved water resistance when compared to an emulsion produced with an 88% hydrolyzed grade of PVOH. Figure 10 shows the difference in cloth-to-cloth wet tensile strength for lightly formulated emulsions produced with either Selvol Polyvinyl Alcohols 418 or 523 as the protective colloid. A vinyl acetate emulsion produced with Selvol PVOH 418 exhibits a minimum 1 PLI improvement in wet tensile over an emulsion produced with Selvol PVOH 523.

FIGURE 12: Improved Compatibility of Emulsions Produced Using Selvol 418 PVOH as the Protective Colloid with Post-Added PVOH

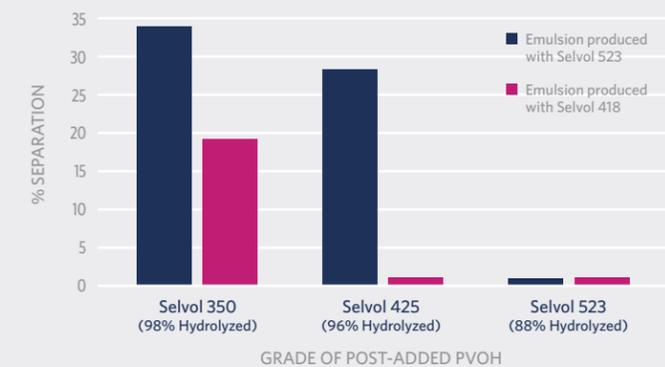


FIGURE 11: Effect of Hydrolysis Level on the Rheological Behavior of the Emulsions (PVOH Degree of Polymerization ffi 1200, i.e. Medium Viscosity)

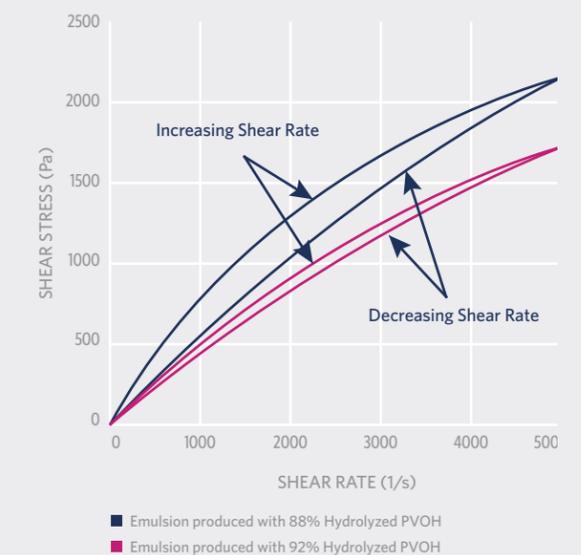
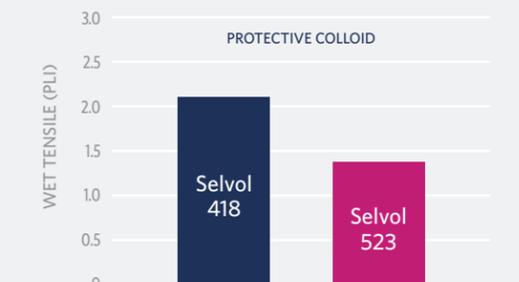


FIGURE 13: Improved Wet Tensile Strength for an Emulsion Produced with Selvol 418 vs. Selvol 523 PVOH



\* PLI = Pounds per Linear Inch  
 \*\* Vinyl acetate homopolymer emulsions formulated with only 15 parts Benzoflex® 9-88 and 1 part Selvol 350.  
 \*\*\* One hour water soak at 25°C

## Selvol PVOH 800 Grades for Emulsion Polymerization

Selvol PVOH 800 grades are improved versions of standard Selvol PVOH grades used for emulsion polymerization. They offer several advantages over standard PVOH grades, including improved solubility and reduced foaming (Table 9).

The enhancements of the Selvol PVOH 800 grades help to reduce polymerization induction time and improve heat transfer. They also result in the production of emulsions with lower coagulum content and a more consistent, reproducible viscosity. The typical properties for Selvol Polyvinyl Alcohols 805,823 and 840 are identical to those for Selvol Polyvinyl Alcohols 205,523, and 540, respectively. This characteristic allows easy substitution of these materials in formulations containing our standard PVOH grades.

The improvement in solubility of the Selvol PVOH 800 grades is shown in Figure 12. Attempts to dissolve the different grades of PVOH at 25 °C for one hour result in Selvol PVOH 823 being almost completely dissolved, while Selvol PVOH 523 is only partially dissolved, as measured by % solids. Another indication of the improved solubility of Selvol PVOH 823 over Selvol PVOH 523 is the amount of undissolved PVOH in the solution, measured as % Gels. Gels may register as soluble material, but in fact are soft, translucent particles of incompletely dissolved polymer. The % Gels of the materials was measured as the amount of material which could not be filtered through a 325 mesh filter after two hours at 25 °C. Selvol PVOH 523 has approximately a 4% higher gel content than does Selvol PVOH 823. Although the result of this laboratory test shows almost complete dissolution of Selvol PVOH 800 grades at room temperature, this is not recommended in production. To ensure complete dissolution, please refer to the procedures outlined in our Selvol Polyvinyl Alcohol Solution Preparation Guidelines brochure.

Because Selvol PVOH 800 grades contain a proprietary dispersant/defoamer, aqueous solutions of these materials foam less than aqueous solutions of their standard grade counterparts. Foaming was evaluated using a high speed Waring blender and a 10% solids PVOH aqueous solution. The solution was agitated in the blender for 10 minutes and then poured into a graduated cylinder. The foam density was then measured after 60 minutes. The Selvol PVOH 823 solution was almost completely devoid of foam, while the Selvol PVOH 523 solution was still extremely foamy (Figure 15). The presence of foam can affect the particle size of the emulsion and also slow down initiation of the polymerization because of air entrapment.

TABLE 9: Comparison of Selvol 800 Grades vs. Standard PVOH Grades

Features	Selvol PVOH 800 Grades <sup>1</sup>	Standard Selvol PVOH Grades 2
Improved Cold Water Solubility	X	
Low Foaming	X	
Reduced Gel Content	X	
Reduced Dusting	X	
FDA Status	X	X
Clear Solution 3		X

<sup>1</sup> Selvol PVOH 805, 818, 823, 830 and 840.

<sup>2</sup> Selvol PVOH 502, 203/E 203, 504, 205/E 205, E 8/88, 513, 518, 523/E 523, and 540, partially hydrolyzed grades. Including partial grades Selvol PVOH E 4/88 LA (low ammonia), E 5/88 LA (low ammonia).

<sup>3</sup> Solutions made with the Selvol PVOH 800 Grades have a slight haze. This is not an indication of PVOH insolubility; in fact, the Selvol PVOH 800 grades exhibit better solubility than do their standard grade counterparts.

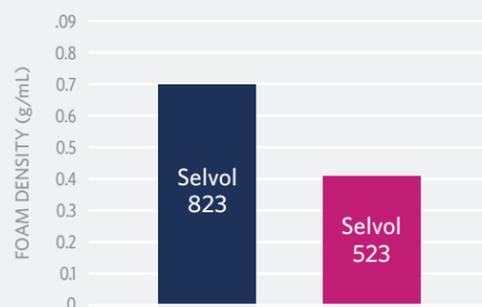


FIGURE 14: Improvement in Solubility of Selvol 800 PVOH Grades over Standard PVOH Grades



\* Solubility based on dissolving material at 25°C for one hour to produce 10% solids aqueous solution.  
\*\* % Gels were measured after dissolving the material for two hours at 25°C

FIGURE 15: Comparison of the Foam Density of Aqueous Solutions of Selvol 823 and Selvol 523 PVOH



\* Higher foam density indicates less foam.  
\*\* 60 minutes after agitation in a Waring 7011 blender Model 31BL92.

## Hints for using PVOH as a Protective Colloid in Emulsion Polymerization

The effective use of PVOH as a protective colloid in emulsion polymerization requires the selection of the appropriate grade of PVOH and the appropriate process conditions. By combining the appropriate grade of PVOH and process conditions, one can produce emulsions with the desired properties for a given application, while minimizing batch-to-batch variability. In some instances, small changes in the process conditions and/or amounts of raw materials being charged to the reactor can produce differing emulsion properties such as viscosity and coagulum levels. Table 9 illustrates how these conditions can affect the emulsion properties.

### DRY AND WET STRENGTH

To ensure consistent performance from PVOH as a protective colloid, one must first make sure that it is properly dissolved and that the proper amount is used. Complete dissolution of PVOH is achieved by following the procedures outlined in the Selvol Polyvinyl Alcohol Solution Preparation Guidelines. Incompletely dissolved PVOH means less PVOH is available to stabilize the emulsion. This may result in a less stable emulsion exhibiting a high coagulum level and low emulsion viscosity. Inversely, a high emulsion viscosity may result from a high PVOH content.

### BLENDED SELVOL PVOH GRADES

When combinations of PVOH grades are used to achieve the desired emulsion properties, care must be taken to ensure that the correct ratio is used. Differences in the amounts of high or low molecular weight grades can affect emulsion viscosity. Too much of a high molecular weight grade of PVOH will cause the emulsion viscosity to be high. Differences in hydrolysis level will also affect emulsion viscosity (see Table 7 and Figure 7), as well as the stability of the emulsion. If too much of a high hydrolysis grade of PVOH is used to produce the emulsion, the emulsion viscosity will be low, and the emulsion may have higher coagulum levels.



### PROCESS VARIABLES

Process variables such as the temperature of initiation, run temperature, reaction time, and the type of initiator can impact the final emulsion properties, especially emulsion viscosity. When comparing emulsion viscosity, one must compare viscosities at equal solids levels. High emulsion solids levels result in higher viscosities. In addition to the solids loading of the emulsion, the particle size and particle size distribution play an important role in determining the emulsion viscosity. Process parameters that can affect the particle size are the initiation temperature, the type of initiator used, and the grade of PVOH used as the protective colloid.

### USING HIGHER HYDROLYSIS GRADES OF SELVOL PVOH

The use of high hydrolysis grades of PVOH results in the production of emulsions with larger particle sizes and lower viscosities than emulsions produced using partially hydrolyzed grades of PVOH. Because PVOH also grafts to the surface of the emulsion particle to provide stabilization, changes in initiator type, or in process variables that may affect the efficiency of the initiator, will impact the grafting efficiency of the PVOH and its ability to stabilize the emulsion polymer particles. These types of process changes can also affect the particle size of the emulsion and result in differences in emulsion viscosity and possibly coagulum levels.

TABLE 10: The Effect of Process Conditions on Final Emulsion Properties

Condition	High Coagulum	High Emulsion Viscosity	Low Emulsion Viscosity
Low Emulsion Solids			X
High Emulsion Solids		X	
Low PVOH Content	X		X
High PVOH Content		X	
Too Much Low MW PVOH	X		X
Too Much High MW PVOH		X	
Too Much High Hydrolysis Level PVOH	X		X
Too Much Low Hydrolysis Level PVOH			X



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