SEKISUI

The Optical Brightener Carrier of Choice in Paper / Paperboard Coatings

SELVOL™
POLYVINYL ALCOHOL

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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.

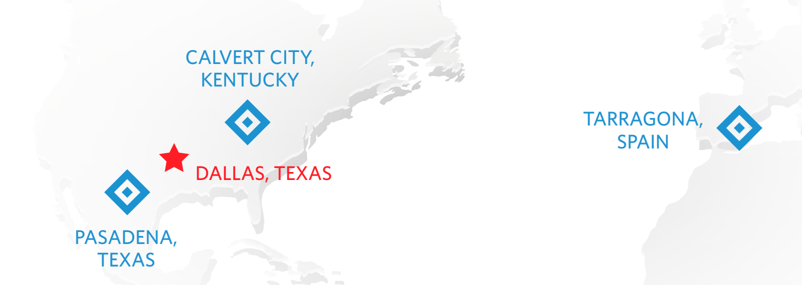

Housing

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 is intended to identify recommended PVOH Grades for use of an Optical Brighteners. 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, 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.

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

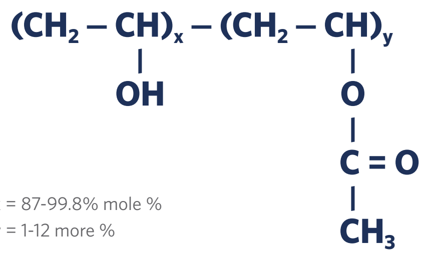
Ingredient	CAS Number
Selvol Polyvinyl Alcohol • Super and Fully Hydrolyzed • Partially and Intermediate Hydrolyzed	 9002-89-5 25213-24-5
Water	7732-18-5
Methanol	67-56-1
Sodium Acetate	127-09-3

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



x = 87-99.8% mole %
y = 1-12 more %

TABLE 2:
Selvol Polyvinyl Alcohol Molecular Weight

Viscosity[1] (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

1 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.

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Selvol Polyvinyl Alcohol Properties

WATER RETENTION

As a hydrophilic polymer, PVOH exhibits excellent water retention properties. Figure 3 compares a low viscosity PVOH (Selvol Polyvinyl Alcohol 103) with other hydrocolloids using the dynamic ABO AKADEMI methodology. In this comparison, polyvinyl alcohol performed well against alginate, polyacrylates and CMC at the low addition levels typical of a water retention aid, indicating that expensive hydrocolloids may be substantially reduced when employing PVOH as an OB carrier.

STRENGTH

Polyvinyl alcohol is widely recognized as the strongest binder in the paper industry. It exhibits superior IGT pick, Mullen burst, Instron tensile and MIT fold properties compared with other natural and synthetic binders. The strength of a specific grade of Selvol Polyvinyl Alcohol is determined by its molecular weight (MW) measured as a 4% solution viscosity. Therefore, high viscosity grades like Selvol Polyvinyl Alcohol 165 yield maximum strength.

However, as shown in Figure 2, even the low molecular weight grades recommended for coating formulations exhibit superior strength allowing for a reduction in total binder level (see Table 7). When total binder level is reduced, performance of the pigment is optimized as observed in improvements to sheet gloss, brightness and opacity (when coating over unbleached fibers or low basis weight papers).

FIGURE 2:
Relative Strengths of Paper Binders

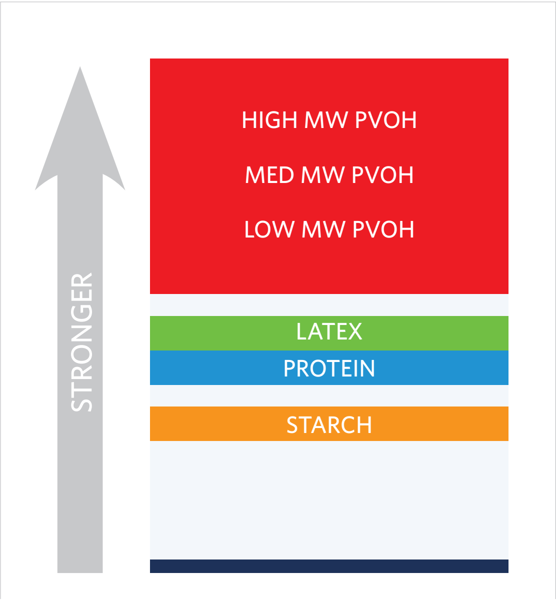
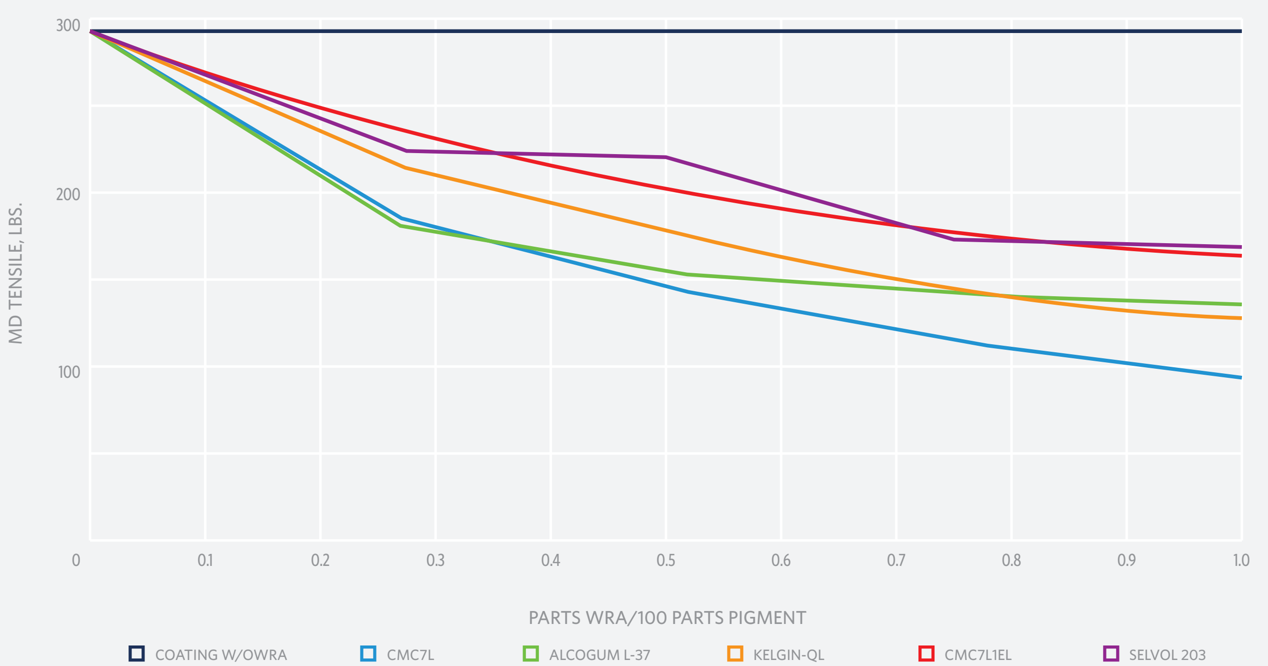


FIGURE 3: PVOH vs. Hydrocolloids - Coating Color Water Retention Aids

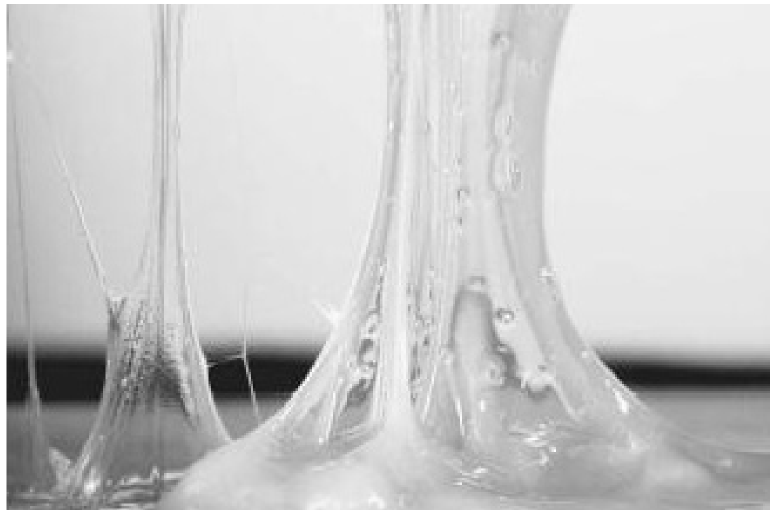
ABO AKADEMI METHODOLOGY - FORMULATION: 100 PTS. #1 Clay, 12 PTS. VINAC 884, X PTS. WRA at 65% Solids



Polyvinyl Alcohol Business

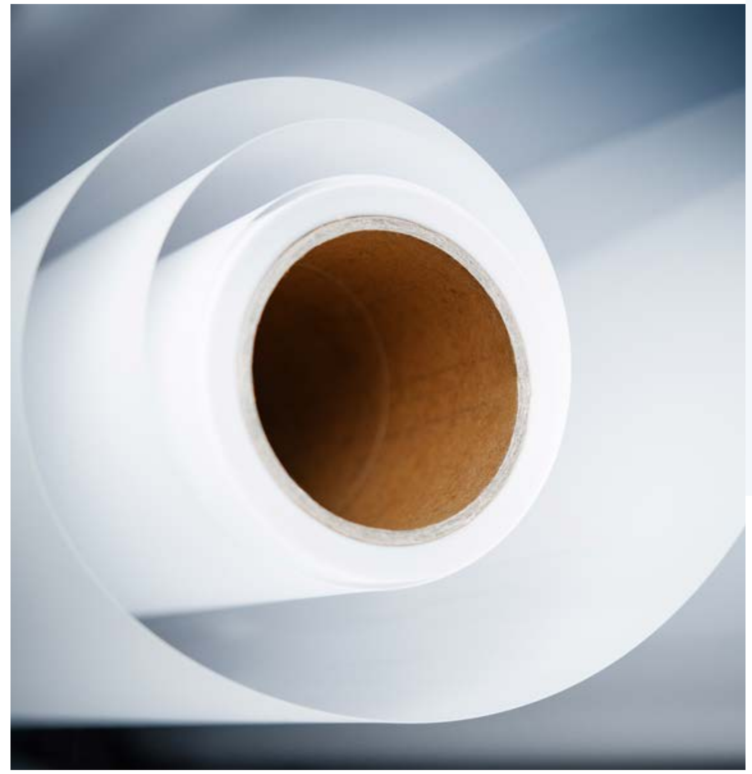
Important end-use markets for these polymer products include textiles, paper, adhesives, building products, and specialty applications.

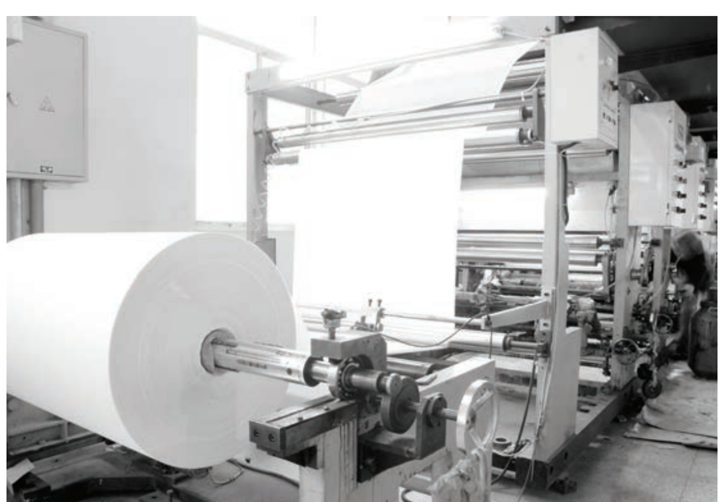
Selvol Polyvinyl Alcohol resins perform well as textile sizing agents, pigment binders, emulsifying agents, and in adhesive and protective film applications. Special properties may be imparted by blending grades or compounding with other ingredients.



Introduction to Optical Brightener

Fluorescent whitening agents, also known as optical brighteners, may be added to coating formulations to increase sheet brightness. Polyvinyl alcohol (PVOH) is recognized worldwide as the most effective “carrier” for optical brighteners. The precise mechanism is not fully understood. One theory proposes an interaction similar to hydrogen bonding which links the optical brightener to the PVOH near the surface of the coating. Another theory proposes that PVOH locks the optical brightener into its active planar or transposition which absorbs UV light and readmits it in the blue-white range of the visible spectrum.





Regardless of the mechanism, by utilizing PVOH as the carrier, it is possible to boost brightness an additional 4+ units. Further, PVOH also provides superior pigment binding strength as well as good water retention properties enabling the coating formula to be optimized for reductions in latex and hydrocolloid levels.

Lastly, when PVOH is added to a coating formula containing optical brightener, a reduction in the low shear Brookfield viscosity is observed. This may allow coatings to be run at higher solids resulting in a quicker immobilization point with reduced binder migration and better coating uniformity.

Brighteners

Low viscosity grades of PVOH, either fully or partially hydrolyzed, are recommended as OB carriers in coating applications as they provide the high shear rheology characteristics required of blade coaters. Also, lower viscosity grades are best suited in developing high solids coating formulations. In addition to our standard Selvol Polyvinyl Alcohol grades which are dissolved in water via a “cooking” process (see our brochure “Solution Preparation Guidelines”), Sekisui also offers a non-cook grade, Selvol Polyvinyl Alcohol 203S, and a ready to use Selvol Polyvinyl Alcohol solution 24-203 (Table 4).

TABLE 4:
Recommended PVOH Grades for Optical Brighteners

Standard Grade	Hydrolysis %	Viscosity (cP)1
Selvol PVOH 203	87.0-89.0	3.5-4.5
Selvol PVOH 103	98.0-98.8	3.5-4.5
Selvol PVOH 107	98.0-98.8	5.5-6.6
Non-Cook Grade	**Hydrolysis %**	**Viscosity (cP)1**
Selvol PVOH 203S[4]	87.0-89.0	3.5-4.5
Solution Grade	**Solution Solids %2**	**Solution Viscosity (cP)3**
Selvol PVOH 24-203	23.0-25.0	250-1300

[1] 4% aqueous solution, 20°C. [2] Forced Convection Oven, 130°C. [3] Brookfield LVF, 12 rpm, #2 spindle, 27°C.
[4] Selvol PVOH 203S is a fine particle size grade with >99% through an 80 screen.

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Selvol Polyvinyl Alcohol 203S as a Non-Cook OB Carrier

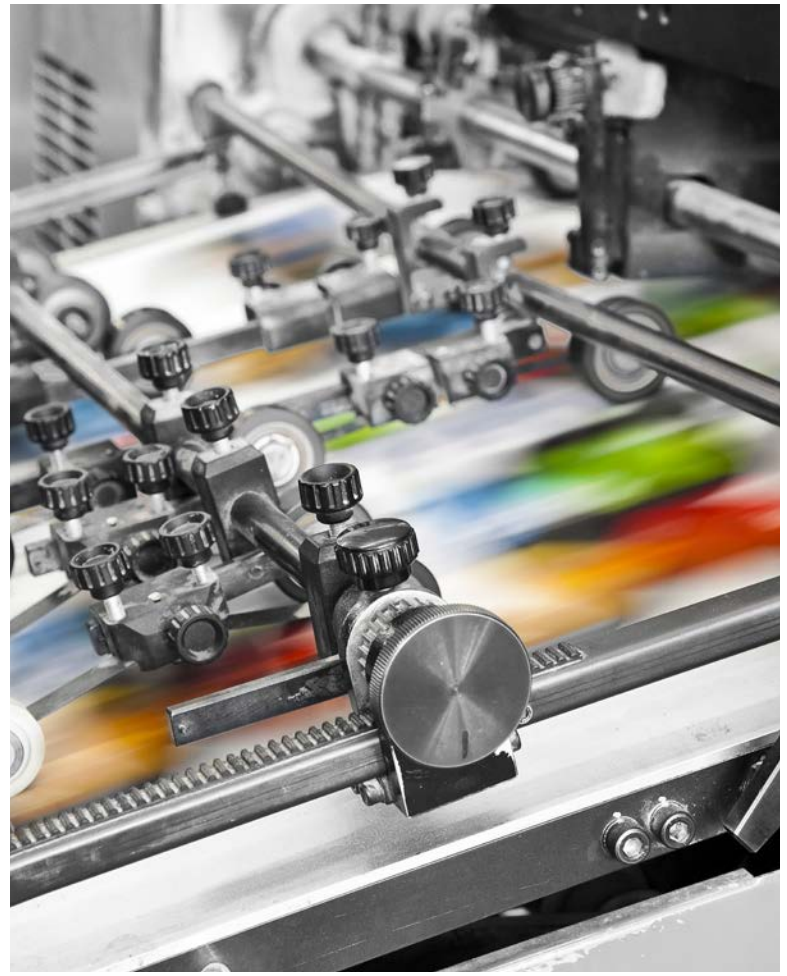
Selvol Polyvinyl Alcohol 203S has been designed to completely dissolve in high-solids aqueous paper coating composition or pigment dispersion. The advantages of adding Selvol Polyvinyl Alcohol 203S as a dry resin include:

- **Higher solids** - the addition of a dry resin facilitates the achievement of maximum coating solids allowing for faster drying and machine speeds.
- **Process simplification** - Avoidance of the "cook-out" (required for standard grades of polyvinyl alcohol) eliminates a processing step and saves time, steam energy and labor cost.

The concept of using Selvol Polyvinyl Alcohol 203S in coating color formulations as a "non-cook" product, either as a pigment binder or as a carrier for optical brighteners, is described in U.S. patent 5,057,570, assigned to Sekisui.

RECOMMENDED MIXING PROCEDURE:

In this procedure, the Selvol Polyvinyl Alcohol 203S resin is added directly into pigment dispersion or into a pigmented formulation while under high shear agitation. It is then mixed for 15 minutes minimum after which the Selvol Polyvinyl Alcohol 203S resin will be totally dissolved.



Directions for recommended use of Selvol Polyvinyl Alcohol 203S are as follows:

1. Kady or Cowles mixers are preferred.
2. Selvol Polyvinyl Alcohol 203S should not be added directly into a high solids pigment dispersion (70+%) because this may cause an unacceptable viscosity increase. Rather, first dilute the pigment dispersion by adding any available dilution water and/or water-based binders (latex, starch, etc.), then add the Selvol Polyvinyl Alcohol 203S.
3. Mix the solution for 15 minutes minimum. Although heat is not required for total solubility, any heat that is generated, either through shear mixing forces or through the addition of hot starch solutions, will increase the rate of solubility of the Selvol Polyvinyl Alcohol 203S.
4. Selvol Polyvinyl Alcohol 203S is, by design, a very fine particle size resin, and it will tend to cause dust during the addition process. Proper ventilation and the use of dust respirators are both recommended.

Selvol Polyvinyl Alcohol Solution 24-203

Selvol Polyvinyl Alcohol Solution 24-203 is an approximate 24% solids solution of Selvol Polyvinyl Alcohol 203 partially hydrolyzed. The product contains a defoamer/biocide system to enhance performance and extend the shelf life. The typical properties for Selvol Polyvinyl Alcohol Solution 24-203 are identical to those of Selvol Polyvinyl Alcohol 203, allowing easy substitution and evaluation in existing formulations.

SOLUTION BENEFITS

Selvol Polyvinyl Alcohol standard grades must be dissolved prior to use. Selvol Polyvinyl Alcohol Solution eliminates the dissolution step and offers a number of advantages, including:

- Ready-to-use
- Improved solution consistency
- Lower energy and processing costs (no cooking required)

STORAGE

Selvol Polyvinyl Alcohol Solution 24-203 should be stored and handled at temperatures between 70° and 100 °F (21 °-40 °C). Storage at lower temperatures (below 65 °F, 18 °C) can cause an increase in solution viscosity and gel formation. At temperatures above 100 °F, Selvol Polyvinyl Alcohol Solutions 24-203 must be covered or enclosed to prevent loss of water, which could result in surface skin formation.

PACKAGING AND SHIPPING

Selvol Polyvinyl Alcohol Solution 24-203 is shipped in 55 gallon drums, 275 gallon intermediate bulk containers, and tank trucks.

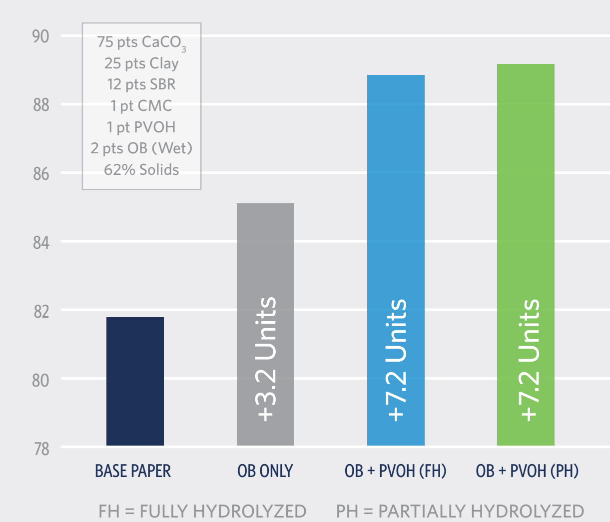


FIGURE 4:
Optical Brightener Enhancement with PVOH
Laboratory CLC Coater Study/3000 FPM

Influence of PVOH Hydrolysis on Optical Brightener Response

As mentioned earlier, low viscosity grades are recommended as OB carriers in coating formulations due to their high shear rheology characteristics. However, with regard to hydrolysis, it has been our experience that partially (87.0-89.0%) or fully (98.0-98.8%) hydrolyzed grades perform equally well.

As shown in this cylinder laboratory coater study (Figure 2), the addition of 2.0 wet parts optical brightener resulted in a gain of 3.2 brightness units. When combined, 2.0 wet parts optical brightener with 1.0 dry part PVOH, brightness improved by a total of 7.2 units or an additional 4.0 units over the optical brightener alone. This was true for both fully hydrolyzed and partially hydrolyzed PVOH.

Use of PVOH with Optical Brighteners in Board Coatings

The trend in bleached board coatings over the past several years is to replace a portion of the fine particle size clay utilized in the topcoat with fine particle size calcium carbonate (CaC03). This has resulted in a brightness increase from 79-81 units with the all clay topcoats to 84-86 units with the clay/CaC03 blends. With FDA approval of certain tetrasulfonated optical brighteners*, brightness can be increased even further. However, the FDA clearance limits addition to approximately 0.75 wet parts of optical brightener per 100 dry parts of pigment which allows for only modest brightness gains. PVOH, which has a synergistic effect with optical brighteners, can be used to further boost and maximize brightness.

To illustrate the effect of PVOH on optical brightener response in typical board coatings, the following study was performed. A series of topcoats with PVOH varying from 0-3 pph was formulated with total binder level kept constant. The topcoats, listed in Table 5, were applied to a 120#/3000 sq. ft. (10 pt) SBS base-sheet on a CLC-6000 coater equipped with a blade metering head. A common basecoat (also shown in Table 5) was utilized with a weight target of 6.0 +/- 0.5 #/3000 sq. ft. The experimental topcoats were applied to the base-coated board also at an approximate coat weight of 6.0 +/- 0.5 #73000 sq. ft.

** Benzenesulfonic acid, 2,2'-(1-2-ethenediyl) bis[5-[[4-[bis(2-hydroxyethyl) amino]-6-[(4-sulfophenyl) amino] -1,3,5-triazin-2-yl] amino]-, tetrasodium salt (CAS Reg. No.16470-24-9); manufactured by Bayer Corporation, Ciba Specialty Chemicals Corporation and Clariant Corporation.*

TABLE 5: Use of PVOH with Optical Brighteners in Board Coating

	Basecoat	Topcoat 1	Topcoat 2	Topcoat 3
Coarse $CaCO_3$	100	-	-	-
Fine # 1 Clay	-	100	70	40
Fine $CaCO_3$	-	0	30	60
Total Binder	15	17	16	16
Vinac® 828M	15	14 - 17	14 - 17	14 - 17
Selvol PVOH 203S	-	0 - 3	0 - 3	0 - 3
Tetrasulfonated OB		0 - 0.75	0 - 0.75	0 - 0.75
Acrylic Thickener	0.2	*	*	*
Target Solids (%)	68	62	64	65
Target Brookfield Viscosity (cP)	2000	2500	2500	2500
Target pH	8.5 - 9.0	8.5 - 9.0	8.5 - 9.0	8.5 - 9.0

* As needed to achieve viscosity targets

Coated sheets were TAPPI conditioned, gloss calendered (175 °F/ 300 pli) and then reconditioned per TAPPI procedures prior to testing. Brightness and fluorescence of the coatings were measured and are shown in Figures 5 and 6, respectively.

As can be seen: Brightness in all pigment compositions followed the same trend:

- Brightness improvements of 1.7-2.0 units can be achieved with OB alone
- An additional 1.0-1.2 brightness units can be achieved by including 1 pph Selvol Polyvinyl Alcohol
- Higher PVOH levels will further increase brightness; for example, 2.0-2.3 brightness units can be achieved by including 2.0-2.5 pph Selvol Polyvinyl Alcohol

Fluorescence results show the same trends as brightness results for all pigment compositions:

- Fluorescence improvements of 1.9-2.3 units can be achieved with OB alone
- An additional 0.8-1.4 fluorescence units can be achieved by including 1 pph Selvol Polyvinyl Alcohol
- Higher PVOH levels will further increase fluorescence, for example, 3.5-4.0 fluorescence units can be achieved by including 2.0-2.5 pph Selvol PVOH

Formulas containing 2.0-3.0 pph PVOH will show a slight reduction in NPA slope and ink transfer compared to all latex formulas at the same total binder level. However, the topcoats containing 2.0-3.0 pph PVOH will also show superior IGT pick strength compared to all latex formulas, allowing a reduction in total binder level. Reducing total binder level will address the deficiencies in ink transfer as illustrated in the following example:

A series of topcoats containing 2 pph Selvol Polyvinyl Alcohol 203S in a 40/60 clay/CaC03 formula (Table 4/topcoat 3) was evaluated. Total binder levels were varied from 14-16 pph. An all latex (Vinac 828M) formula was also run for comparison. The coatings were applied and tested per the conditions cited above. The test results, listed in Table 6, show the following:

- Addition of 2 pph of Selvol Polyvinyl Alcohol slightly reduces NPA ink transfer and slope compared to the all latex formulas at the same total binder level
- Addition of 2 pph of Selvol Polyvinyl Alcohol allows a reduction of 1 -2 pph total binder compared to the all latex formula
- The reduced binder formulas containing Selvol Polyvinyl Alcohol show comparable IGT pick, NPA ink transfer and slope compared to the all latex formula

TABLE 6:
Reduction of the Total Binding Level/Test Results

	A	B	C	D
Total Binder Level (pph)	16	16	15	14
PVOH Level (pph)	0	2	2	2
Brightness (%)	84.9	88.5	88.7	89.0
Fluorescence (%)	0	3.7	3.85	3.66
IGT Pick (VVP)	146	179	165	149
NPA Ink Transfer (%)	59.9	46.6	56.8	62.4
NPA Slope (g/cm/s)	11.4	6.9	8.5	10.9

FIGURE 5:
Brightness vs. PVOH Level

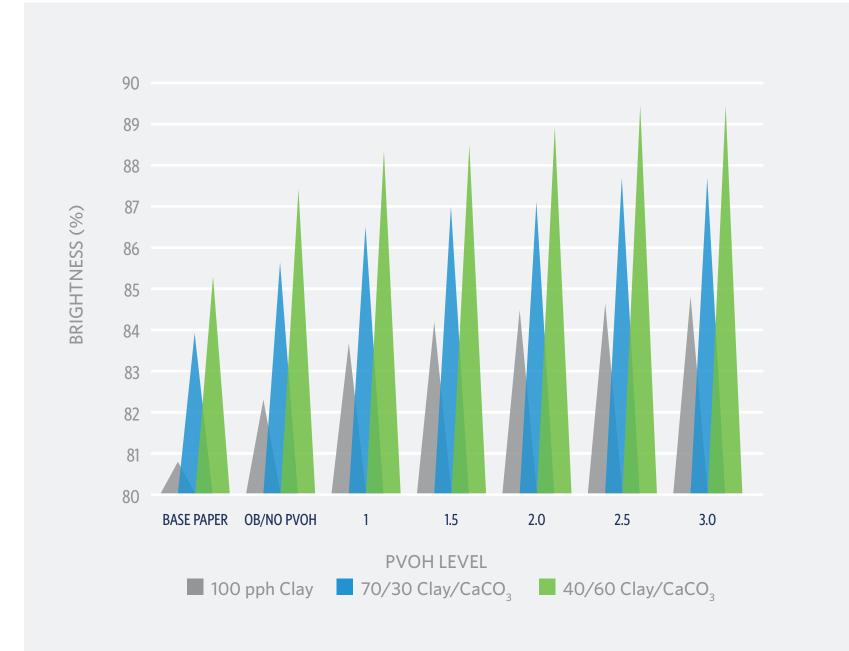
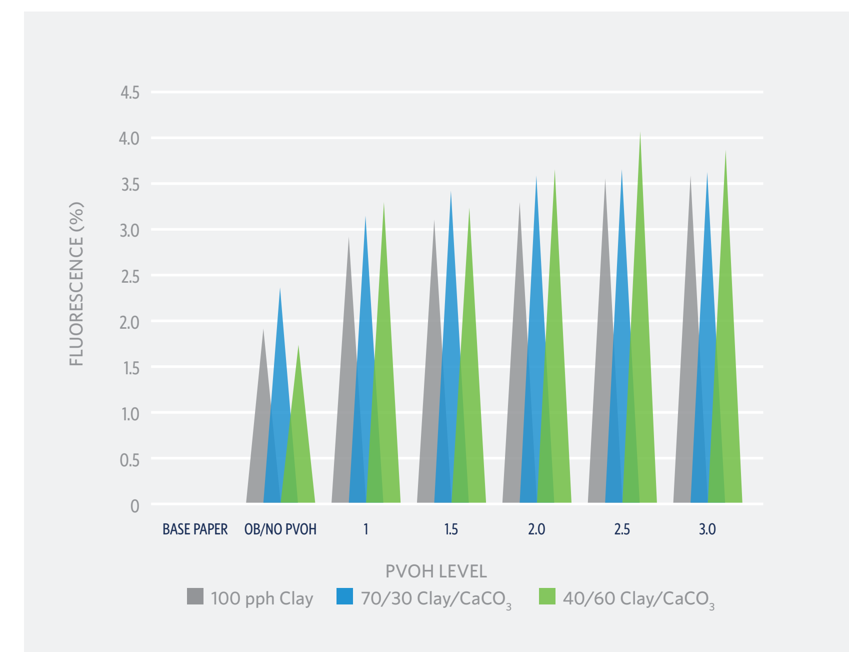


FIGURE 6:
Brightness vs. PVOH Level



Rheological Synergy of PVOH with Optical Brighteners

Beyond the higher brightness response obtained when PVOH is used with optical brighteners, a low shear viscosity reduction synergy also exists between these two materials. This synergy is especially prominent in high calcium carbonate containing coatings and less pronounced in high clay containing coatings. If either the PVOH or optical brightener is added on its own, an increase in low shear viscosity is typically observed.

However, when both are added to a coating formula, the low shear Brookfield viscosity could decrease by as much as 40%, depending on the addition level of the optical brightener and PVOH. High shear viscosity will increase regardless in direct proportion to the level of PVOH when compared to a coating which does not contain PVOH.

TABLE 7:
Rheological Synergy of PVOH with Optical Brighteners

Ingredient	Dry Parts
$CaCO_3$	80
Clay	20
Latex (vinyl acetate)	12
CMC**	0.5
PVOH	Selvol PVOH 203S
Optical Brightener	Hexasulfonated*

* Low shear viscosity reduction was also observed with tetrasulfonated OB, however, the reduction was somewhat less than with the hexasulfonated OB.
** Carboxymethyl Cellulose.

This low shear viscosity reduction is particularly useful when Selvol Polyvinyl Alcohol 203S is used as a dry add material. The combination of viscosity reduction and dry addition of Selvol Polyvinyl Alcohol 203S typically allows for an increase in the overall coating solids while maintaining or even lowering the overall Brookfield viscosity as compared to a coating without the Selvol Polyvinyl Alcohol 203S at a lower solids. The increase in coating solids has the benefit of a quicker immobilization point leading to reduced binder migration and better coating uniformity. A potential increase in machine speed is also possible due to a reduced water load.

FIGURE 7:
Low Shear Brookfield Viscosity with Increasing Selvol 203S Additions @ 69% Solids

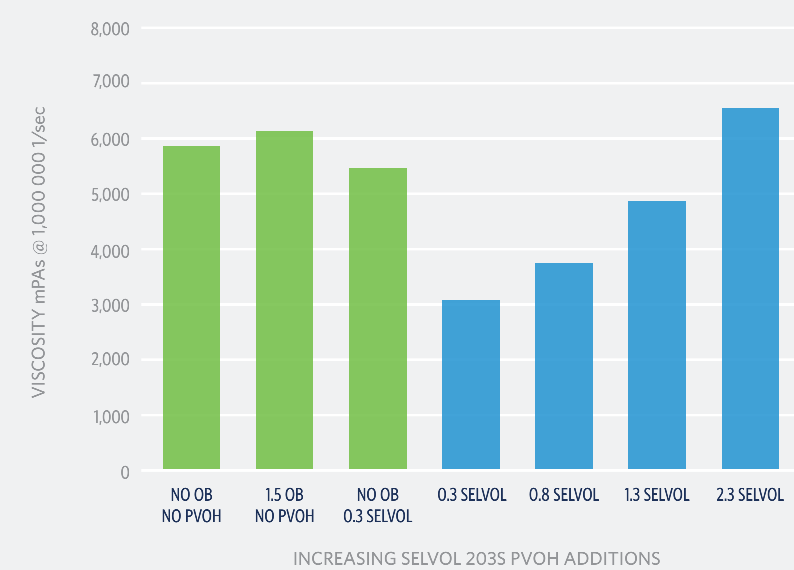


FIGURE 8:
High Shear Brookfield Viscosity with Increasing Selvol 203S Additions @ 69% Solids

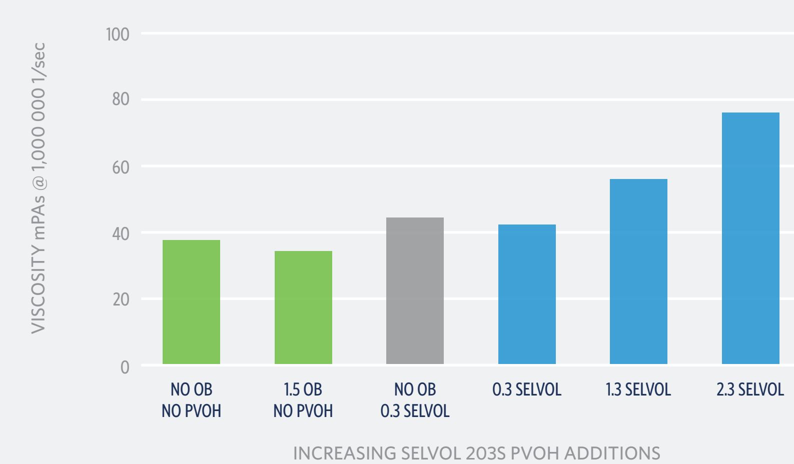


Figure 7 illustrates the low shear Brookfield viscosity of the above coating at 69% solids. Figure 8 illustrates the high shear viscosity of the above coating at 69% solids using a high shear capillary at 1,000,000 1/sec. In both figures:

- The first data point shows the viscosity of the coating without either the OB or PVOH
- The second data point shows viscosity with 1.5 wet parts of OB
- The third data point shows viscosity with 0.3 dry parts of Selvol 203S PVOH
- The remaining data points show viscosity of the coating with 1.5 wet parts of OB and increasing levels of Selvol Polyvinyl Alcohol 203S

SELVOL™ POLYVINYL ALCOHOL

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