

# Rheology Control Of High-Solids Coatings

By Dennis G. Miller, Technical Service Representative,  
William F. Moll, Technical Service Manager, and  
Vaughn W. Taylor, Laboratory Manager  
Cabot Corporation, Tuscola, Ill.

**D**UE TO FEDERAL regulations limiting the emission of organic solvents from surface coatings operations, the paint industry is in the process of reformulating many of its products. Four approaches are possible: high-solids solvent borne coatings; water borne coatings; powder coatings; and radiation-cured coatings. Marketing data for the last two years show that high-solids solvent borne coatings are gaining acceptance in many broad areas of usage including metal furniture, automotive topcoat, can coatings, and flat stock.

The coatings industry has experienced two major rheology related problems in the development of suitable commercial high-solids coatings. These are film sagging during the heat cure cycle and excessive pigments settling during storage.

Both problems are related to the replacement of the high molecular weight resins used in conventional solvent coatings with the lower molecular weight resins in the new low solvent high-solids coatings. This formulation change allows the high-solids coatings to meet the new Volatile Organic Content (VOC) limitations set by the Federal government, without the need for further reduction with solvent prior to application.

Conventional coatings using the higher molecular weight resins have higher "package" viscosities and are normally diluted 3:1 or 4:1 with solvent prior to application to bring their viscosity levels down to sprayable values (25 to 50 seconds in a Zahn #2 cup). In contrast, the new high-solids coatings are formulated at these application viscosities.

The film sagging problem, which occurs more frequently with the new high-solids coatings is illustrated in Figure 1.

When a coating is placed in a cure oven, the viscosity and the sag resistance of the film are altered because of three different factors. The increase in temperature reduces the film viscosity while the evaporation of the solvents and later the crosslinking (curing) increases the viscosity.

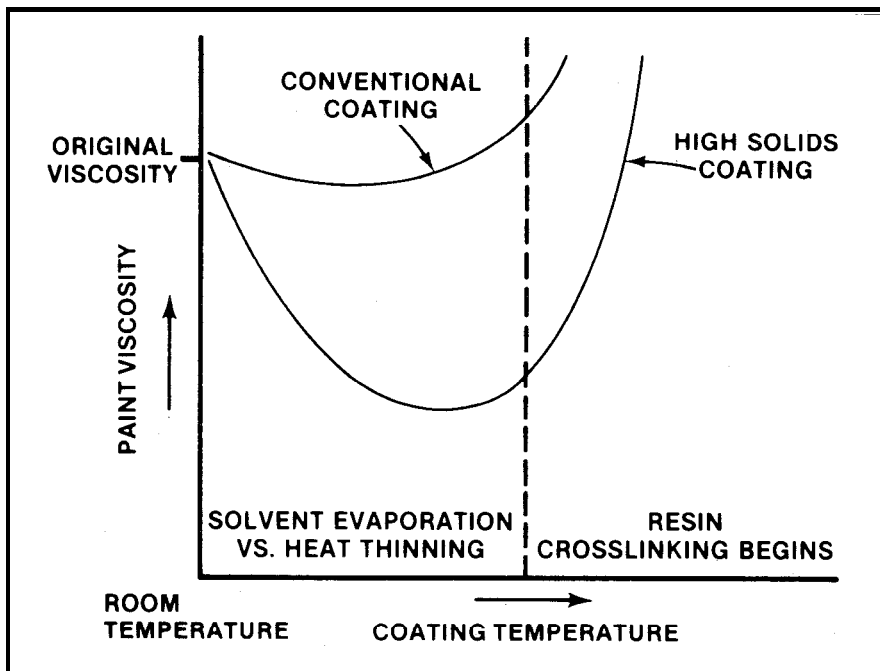


Figure 1. Comparison of viscosity changes during the heat cure of conventional and high solids coatings.

In conventional coatings, as shown in Figure 1, the reduction in viscosity due to temperature rise is counteracted by the increase in viscosity due to solvent loss. This is followed by an increase due to curing; thus, little sagging occurs. In contrast, the lowering of the viscosity by heat far outweighs the rise from solvent evaporation in high-solids coatings. This lowering of viscosity allows significant sagging to occur before the viscosity increase related to curing occurs. The new high-solids coatings show more pigment settling during storage than conventional coatings because of their lower package viscosities.

In many conventional paint formulations both film sagging and pigment settling problems have been solved through the use of a suitable amount of a thixotrope. This thixotrope must provide the proper rheological properties without causing undesirable side effects, such as excessive viscosity build-up or gloss reduction of the cured film.

In this study, we compared the abilities of three types of thixotropes—fumed

silica, precipitated silica, and organo-clay—to impart anti-sag and anti-settling properties to a high-solids polyester baking enamel. Each thixotrope was evaluated in a loading ladder to establish its optimum anti-sag performance level. Once these had been established, the viscosity, gloss, and anti-settling performance of each thixotrope level were measured. Each formulation attaining acceptable anti-sag performance was examined on a Ferranti-Shirley cone and plate viscometer for thixotropy. Also, a new testing device, a yield point tensiometer, was used to determine the yield values of the successful coatings. The information was then used to calculate a maximum theoretical non-sagging dry film thickness.

## Selection of Thixotropes

The fumed silica used in this study had a surface area of 200m<sup>2</sup>/gm and a bulk density of 2.3 to 3.0 lbs./ft.<sup>3</sup> (.37 to .48 g/cm<sup>3</sup>). Fumed silica achieves its special viscosity and thixotropy control proper-

**Table I. Base High Solids Coating**

Grind		
Add in order	Pounds	Gallons
Polyester 5771 <sup>(1)</sup>	181.75	19.89
Ethylene Glycol Monoethylether	30.29	3.74
Surfynol PC <sup>(2)</sup>	1.21	0.15
TiO <sub>2</sub>	333.21	9.51
High speed disperse (lab dispersator 1150 fpm) to Hegman 7.5. Then add under agitation (lab dispersator 300 rpm):		
Let Back		
Polyester 5771	181.75	19.69
Cymel 303 <sup>(4)</sup>	148.00	14.83
VP 451 <sup>(5)</sup>	12.72	1.71
Methyl Ethyl Ketone	30.29	4.52
N-Butyl Acetate	182.48	24.88
N-Butanol	6.06	0.90
10% L-722 <sup>(6)</sup> in N-Butyl Acetate	4.00	0.54
	<u>1110.18</u>	<u>100.00</u>
Formulation Constants		
Volume solids	62.0%	
Weight solids	74.9%	
Volatile organic content	2.83 lbs/gal (340g/L)	

<sup>(1)</sup>Trademark of Cargill Corp.

<sup>(2)</sup>Trademark of Air Products Corp.

<sup>(4)</sup>DuPont R-900

<sup>(5)</sup>Trademark of American Cyanamid

<sup>(6)</sup>Trademark of Byk Mallinckrodt

<sup>(6)</sup>Trademark of Union Carbide Corp.

ties from its unusual surface chemistry and aggregate structure. Fumed silica is produced by vapor phase hydrolysis of pure silicon tetrachloride in a flame of hydrogen and oxygen.

Submicroscopic molten particles of pure silicon dioxide are formed in the flame which collide and fuse with one another to form small branched chain submicron sized aggregates. Some hydrogen chloride is adsorbed on the surface of the silica but is later removed by calcination to a level of less than 200 ppm.

The surface of the fumed silica is populated by three types of chemical groups: the siloxane group; the hydrogen-bonded hydroxyl group; and the isolated hydroxyl group.

The siloxane groups, which cover about 50 percent of the surface, are non-polar and account for the hydrophobic characteristics of the silica surface. The hydrogen-bonded hydroxyls account for about 25 percent of the surface groups. The remaining 25 percent of the surface contains isolated hydroxyls.

The hydroxyl groups are hydrophilic and are the key to the mechanism through which fumed silica functions. When fumed silica is dispersed in a liquid, the hydroxyl groups on adjacent silica aggregates can hydrogen bond with one another to form a three dimensional

silica network throughout the liquid. Thus, the isolated hydroxyls become very important because their only opportunity for hydrogen bonding is with an isolated hydroxyl group of another aggregate.

This silica network can impart three rheological properties to a system: viscosity increase, thixotropy, and yield value. The silica network increases the viscosity of the system. When the system is sheared, the interaggregate hydrogen bonds are broken and the viscosity of the system decreases. After the shearing has ceased, the hydrogen bonds will reform on standing. The silica network rebuilds and the liquid viscosity increases again. This is thixotropy. This property allows the coating to thin under the shear forces of application, and then thicken on the substrate to resist gravitational sag.

The network also imparts the property of yield value, the amount of shear stress required to initiate flow. Unless the gravitational shear stress on a given layer of a coating exceeds this yield value, no flow will occur and sag resistance is obtained. The presence of a yield value retards or eliminates settling of pigment particles.

The organoclay used was dimethyldioctadecylammonium montmorillonite. Organoclays are exceedingly small silicate platelets (2 nm thick, 500 nm

wide) coated with organic molecules via ion exchange. The organoclay functions via an interparticle interaction at the edges of the smectite clay platelets. This interaction allows the platelets to form a network resembling a house of cards. The network gives rise to the development of yield value and thixotropy because the shear can disrupt the interparticle interaction.

The precipitated silica used was a thixotropic grade having a surface area of 225m<sup>2</sup>/gm. Precipitated silicas are prepared by the acidification of aqueous sodium silicate solutions. The shape of precipitated silica aggregates resemble a grapelike cluster of spherical primary particles and has porosity. The surface is fully hydroxylated allowing the surface hydroxyl groups to hydrogen bond among themselves. These two facts combine to make precipitated silicas less effective than fumed silicas in building a network in a liquid system. Typical use levels of two to three times the concentration of fumed silica are required for equal performance.

These thixotropes can be affected by other materials present in the systems in which they are used. All three are affected by the polarity of the solvents present. The greater the polarity of the solvent system, the less effective they all are, the organoclays being the most affected. Materials which have active hydrogen bonding sites can affect the silicas. Mono-functional materials will act as "chain terminators" degrading the performance of the silicas. Poly-functional materials will act as "chain propagators" and enhance the performance of the silicas.

#### Formulation and Preparation

The high-solids coating chosen to evaluate the three thixotropes was a state-of-the-art general purpose formulation based on 5771<sup>1</sup> polyester resin crosslinked with Cymel 303<sup>2</sup>, hexamethoxymethylmelamine. This base coating has a VOC of 2.8 pounds of solvent per gallon of coating (340g/L) and a viscosity of 22 seconds on a Zahn #2 cup. The VOC fits many end use categories—metal furniture, automotive topcoats, and miscellaneous metal parts—and the viscosity is suitable for conventional application equipment. The base formulation and its constants are given in Table I.

Each thixotrope was included in the grind of the coating to obtain the optimum performance.

The precipitated silica was added to and dispersed with the titanium dioxide

**Table II. Evaluation of Thixotrope Levels**

Wt % and Type of Thixotrope	Additives Present	Viscosities			Sag		Settling	Gloss		Commercial Acceptability of Formulation	
		Brookfield 6 rpm cPs (mPa.s)	60 rpm cPs (mPa.s)	Zahn (sec)	Anti-Sag Meter Rating	Spray Panel @1.5 mil (38µm)	Amount & Type	Ease of Redis-persion	60 (%)		20 (%)
None	Yes	59	57	22	2.0	Sagged	1/8" Hard (3mm)	Difficult	97	78	No
1 Fumed Silica 0.35	Yes	75	75	25	2.5	Very Slight Sag	None	.	95	74	Yes
2 Fumed Silica 0.17	Yes	61	61	23	2.5	Slight Sag	None		94	74	Yes
3 Organoclay 0.50	Yes	80	71	22	2.0	Sagged	1/16" soft (1.5mm)	Easy	86	51	No
4 Organoclay 0.75	Yes	70	73	23	2.0	Bad Sag	1/16" soft (1.5mm)	Easy	63	20	No
5 Silica 0.65 ppt.	Yes	83	73	25	2.5	Bad Sag	1/8" Hard (3mm)	Moderate	92	61	No
6 Silica 0.98 ppt.	Yes	155	120	23	2.5	Slight Sag	1/8" Hard (3mm)	Moderate	88	52	No
7 Silica 1.63 ppt.	Yes	155	136	27	1.5	Slight Sag	1/8" Hard (3mm)	Moderate	77	26	No
8 None	No	72	72	23	2.5	Sagged	1/8" Hard (3mm)	Difficult	99	88	No
9 Fumed Silica 0.35	No	165	130	31	2.0	No Sag	None	—	97	76	Yes

<sup>0</sup>Surfynol PC and 1-722

to a Hegman reading of 7.5. At lower dispersion levels the precipitated silica results in excessive gloss reduction in the cured film.

The organoclay was pregelled according to the manufacturer's procedure—a 13 wt. percent concentration in VM&P naphtha with methanol (95 percent alcohol, 5 percent water) added at a level equal to 30 percent of the weight of the organoclay. The pregel was added to the grind and dispersed with the titanium dioxide to a Hegman reading of 7.5. The organoclay formulations were adjusted to maintain the VOC at 2.8 by removing sufficient normal butyl acetate from the "letback" to balance the solvent in the organoclay pregel.

In the case of the fumed silica, the titanium dioxide was dispersed to a Hegman reading 7.5 and then the fumed silica was added. The dispersion was then mixed to obtain a Hegman reading of 5.5 to 6.0. The fumed silica is sensitive to overshearing and should be dispersed only to a 5.5 to 6.0 Hegman reading for maximum thixotropic development. Overshearing will break down the structure of the fumed silica, lowering the amount of network formation and reducing the sag and settling resistance of the formulation. Each coating was letback in the same manner listed in Table I.

Two coatings were prepared without the two additives—Surfynol PC<sup>0</sup>, a bubble breaker, and L-722<sup>4</sup>, a flow control agent. This was done to judge the effects of these additives on the anti-sag, anti-

settling, viscosity, and gloss of the coatings. The base formulation without any thixotrope and a coating containing 0.35 wt. percent fumed silica were used for this test.

### Test Results

Anti-sag performance was evaluated in two ways. Panels were prepared using a low range Leneta Anti-Sag meter, a draw-down blade with graduated notches from 1 to 6 roils deep in 0.5 mil steps (25 to 150 µm in 12.5 µm steps). Coatings were drawn down on cold rolled steel panels and then flashed at room temperature for five minutes in a vertical position. Then the panels were baked in a vertical position for 20 minutes at 300 F to cure the coating. The panels were rated by noting the maximum film thickness which did not sag across the gap to touch the next highest/thickness band.

Coatings were air sprayed with a Binks Model 18 hand gun on cold rolled steel panels. Immediately after each panel was sprayed, a small flat-ended spatula was drawn across the panel to create a paintless band with a bead of paint at the upper and lower edges. These panels were then flashed and cured as mentioned above. The panels were prepared at dry film thicknesses of 1.5 ± 0.1 roils (38 ± 2 µm).

The Leneta Anti-Sag meter results do not correlate very well with the spray panel results. The draw down application does not subject the coating to the

same high shear rate as an air spray gun (estimated to be in the range of 10,000 sec.<sup>-1</sup>). Also, the Anti-Sag meter method does not cause the loss of solvent in application that the spraying does. Because most industrial coatings are sprayed, emphasis is on the results of the sprayed panels.

The coating containing 0.35 wt. percent fumed silica gave the best sag resistance at 1.5 roils (38 µm). This was followed by the coating containing 0.17 wt. percent fumed silica. The coatings with 1.63 wt. percent and 0.98 wt. percent precipitated silicas were almost as good in sag performance. The coatings with organoclay levels of 0.5 and 0.75 wt. percent and the 0.65 wt. percent precipitated silica fared worse than the control without thixotrope.

The effect of the surface active agents are evident in coatings 8 and 9 (Table II). The sag performance of these coatings was better than the control and coating 1, their counterparts containing the additives.

The anti-settling behavior was determined by allowing the material to sit undisturbed for 45 days. Each sample was then judged for the amount and the ease of redispersion on any settled material.

The control coating experienced 1/8-inch (3mm) of hard settling, which was difficult to redisperse. It required high speed mixing to reincorporate the settled pigment. The precipitated silica coatings also experienced 1/8-inch (3 mm) of hard settling, which required moderate mixing for reincorporation. The organoclay

**Table III. Yield Point Tensiometer Study of High-Solids Coatings**

Yield Values (dynes/cm <sup>2</sup> )		
Solids Cone. in Coating wt. %	Control	0.35 wt. % Fumed Silica
75	0.0	0.0
85	0.8	7.4
90	2.3	7.4
	2.3	3.2

**Table IV. Maximum Non-Sagging Wet and Dry Film Thickness Calculated From Yield Values**

Solids wt. %	Control Coatings				0.35 wt. % Fumed Silica			
	wet mils (μm)		dry mils (μm)		wet mils (μm)		dry mils (μm)	
75	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)
80	0.23	(5.8)	0.14	(3.6)	2.13	(54.1)	1.48	(37.6)
85	0.64	(16.3)	0.49	(12.4)	2.06	(52.3)	1.57	(39.9)
90	0.61	(15.3)	0.51	(13.0)	0.86	(21.8)	0.72	(18.3)

coating produced 1/16-inch (1.5 mm) of soft settling, which was easy to remix. The fumed silica coatings produced no settling in the test period. The additives showed no effects on the settling resistance of the coatings.

The viscosities were measured using a Brookfield LVT viscometer with a #2 spindle after 20 minutes at 6 rpm and 5 minutes at 60 rpm. The viscosities were checked also with a Zahn #2 cup. The viscosity increases caused by the thixotropes were minor in most cases. All the coatings were within the ranges. Even the 1.63 wt. percent precipitated silica and its 27 seconds Zahn #2 value is not a significant deviation. The additives, as expected, slightly reduced the viscosities of the coatings due to surface tension effects.

The gloss determinations were run on the 1.5 mil (38 μm) panels used for the sag resistance. The panels were run on a Lockwood and Melore Model AJ3A glossmeter at 20 and 60 degree angles.

The inclusion of all of the thixotropes reduced the gloss values for each of the coatings. The organoclay reduced the 60 degree gloss by 11 to 34 units of reflectance and the 20 degree gloss by 27 to 58 units. The precipitated silica reduced the 60 degree gloss by 5 to 20 units and 20 degree gloss by 17 to 52 units. The fumed silica reduced the 60 degree gloss by 2 to 3 units and the 20 degree gloss by only 4 units.

A loss of 3 to 5 units on the 60 degree gloss and 2 to 4 units on the 20 degree gloss would be acceptable in most coating systems in return for acceptable anti-

sag and settling properties. Only the fumed silica coating meets these criteria.

The additives showed a significant effect on the 20 degree gloss of the coatings. Coating 8 showed a 10 degree increase in 20 degree gloss over the control coating.

The coatings were examined on a Ferranti-Shirley cone and plate viscometer at shear rates from 90 to 440 sec.<sup>-1</sup>. No significant amount of thixotropy was found in any of the coatings.

Upon spray application of the coatings, evaporation of the solvents raises the solids concentration. Two of these coatings were chosen and evaluated at 80, 85, and 90 percent wt. solids to characterize their behavior at a composition closer to the real film deposited on a sprayed panel. The control coating and the coating containing 0.35 wt. percent fumed silica were chosen. The control coating gave a baseline to compare with the thixotrope's performance. The 0.35 wt. percent fumed silica coating gives the best observed sprayed panel sag resistance. Again, measurements of these coatings at shear rates from 90 to 440 sec.<sup>-1</sup> revealed no significant thixotropy.

There were significant differences in the measured yield values of the control coating and the coating containing 0.35 wt. percent fumed silica (Table III). The yield values were determined using a yield point tensiometer which measured the force required to initiate motion in a vertical plate completely immersed in the coating.

The maximum film thickness, X, which the yield value will support with-

out slumping can be calculated from the equation:<sup>5</sup>

$$x = \frac{\text{Yield Value}}{\text{Density} \times \text{Gravity}}$$

The wet film thicknesses that can be supported by the measured yield values were calculated. The corresponding dry film thicknesses are contained in Table IV. The agreement between the predicted film thickness that the yield value will support and the observed sag values are very good. The coatings containing 0.35 wt. percent fumed silica gave good sag resistance at 1.5 mils (38 μm) dry film thickness. The control coating could not be sprayed successfully to obtain 0.5 mils (12.5 μm) dry film thickness. A coating of 0.7 mils (18 μm) dry film thickness was successful but sagged. Although the study was unable to establish a direct correlation for the control coating, the theoretical and experimental sag values are in general agreement.

Based on the performance properties of the coatings containing various levels of the thixotrope studied, only fumed silica provided adequate anti-settling and anti-sag control. Fumed silica also exacted the smallest price in gloss reduction. The additional raw material costs per gallon in using fumed silica at levels of 0.17 and 0.35 wt. percent are low<sup>1</sup>, 5.8 and 12.0 cents respectively.

The theological investigations established two major points. No thixotropy was observed in any of the coatings at 75 percent wt. solids using a Ferranti-Shirley cone and plate viscometer. The control and the coating containing 0.35 wt. percent fumed silica showed no thixotropy when adjusted to 80, 85, and 90 wt. solids to simulate the coating after application.

Yield value was determined to be the major theological property controlling the sag resistance of the high-solids coatings. A simple yield point tensiometer was used to determine the yield points of the selected coatings. The control and the coating containing 0.35 wt. percent fumed silica were tested at 75, 80, 85, and 90 percent wt. solids. Good correlations between the calculated maximum dry film thickness without sag and the observed sag resistance of the coatings were obtained.

#### References

1. Trademark of Cargill Corp.
2. Trademark of American Cyanamid Co.
3. Trademark of Air Products & Chemicals Inc.
4. Trademark of Union Carbide Corp.
5. Patton, Temple C. *Paint Flow and Pigment Dispersion*, John Wiley and Sons, 1979, p. 575.