



Application Information CC-A 5

# Additives for Ambient Curing Polyester Resins

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## Air Release Additives

### Additives Work in Three Steps

#### 1. Displacing air from filler and reinforcement materials

By reducing the interfacial tension between resin and filler/reinforcement materials, the trapped air is displaced into the resin.

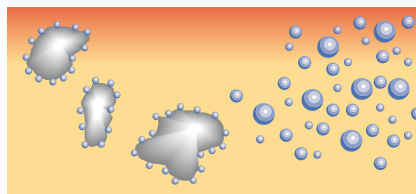
#### 2. Smaller bubbles coalesce to form large bubbles

Bubble-stabilizing substances are displaced by the air release additive. Smaller bubbles coalesce to form larger bubbles, which rise to the surface faster because of their higher buoyancy (Stokes' law).

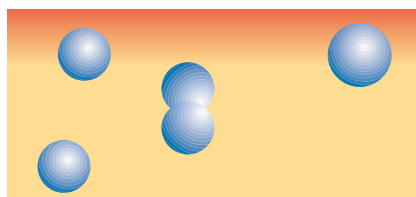
#### 3. Bubbles burst on the surface

Bubble-stabilizing substances are displaced and the bubbles burst.

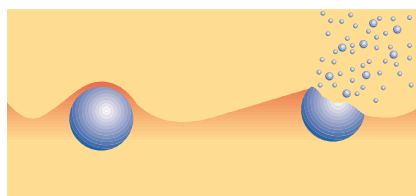
### Air Release Additives Work in Three Steps



Step 1



Step 2



Step 3

figure 1

### Optimized Dosage

BYK air release additives achieve excellent deaeration even at small dosage levels.

### BYK Air Release Additives

#### Air Bubbles

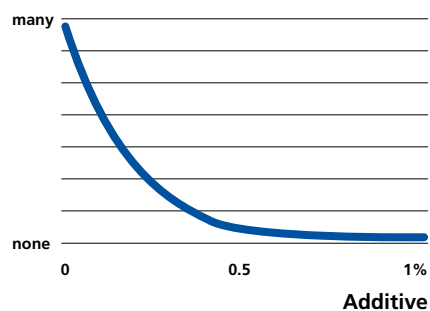


figure 2

## Products

**BYK-A 500** is recommended for transparent systems.

**BYK-A 501** is a universal air release additive with strong incompatibility.

**BYK-A 505** is based on 100 % renewable raw materials.

**BYK-A 515** shows good fiber wetting properties. Recommended for vinylester resins.

**BYK-A 550** is highly effective with minimal haziness.

**BYK-A 555** shows the best air release effects and can be used in most applications.

**BYK-A 560** provides excellent air release with excellent fiber wetting properties.

## Air Release Additives for Unsaturated Polyester Resins

Air Release [%]

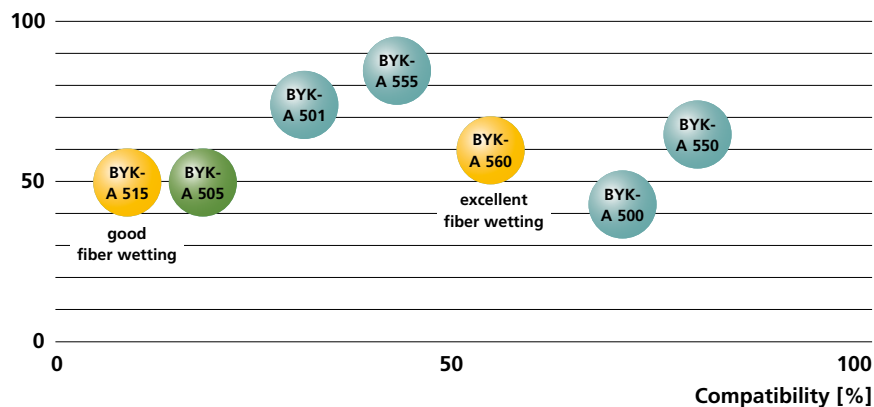


figure 3

## Test Method

This test method makes it possible to visually evaluate air release speed in unsaturated polyester resins.

Pre-mix additive into promoted resin (Dosage: 0.1-0.5 % based on resin).

Add peroxide, agitate under high shear, and whip in as much air as possible for 30 to 60 seconds.

Immediately after agitation, pour the resin into a metal mold. Allow 30 seconds deaeration time, then cover with Mylar film.

After casting is completely cured, remove from the mold, and visually evaluate the air release additive effect.

Whip air into resin  
(high-speed disk)



Cover after 30 seconds



BYK-A 555

without

with



BYK-A 555 at 0.2% in unsaturated polyester resin. Only fast air release speed allows low void content in the final part.

figure 4

## Application Areas

	UP Resins	Fiber Wetting Properties	Gel Coats	Casting	Transparent Parts	Vinylester Resins
BYK-A 500						
BYK-A 501						
BYK-A 505						
BYK-A 515						
BYK-A 550						
BYK-A 555						
BYK-A 560						

■ Excellent    ■ Good

figure 5

## Wetting and Dispersing Additives

### Low Molecular Weight, Polymeric Wetting and Dispersing Additives to Reduce Viscosity

The structure of the classic deflocculating additive has spatially close pigment/filler affinic groups and a resin-like chain structure. Such additives are low molecular weight polymers that adsorb onto the pigment/filler surface. This reduces interactive forces between pigment/filler particles, which, in turn, significantly reduces the viscosity of the filled resin system (figure 6).

### Viscosity Reduction: BYK-W 909, BYK-W 985, BYK-W 969

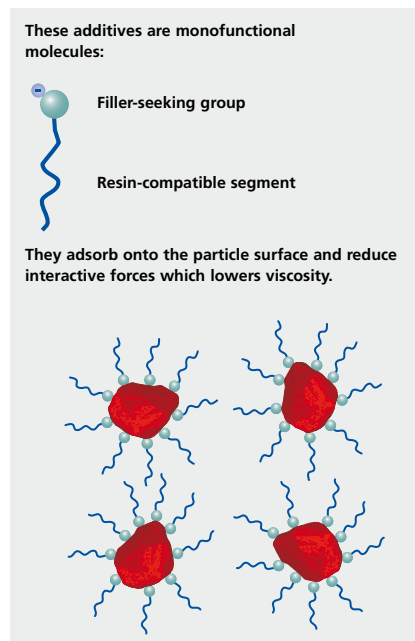


figure 6

### Viscosity Reduction and Anti-settling: BYK-W 980, BYK-W 966

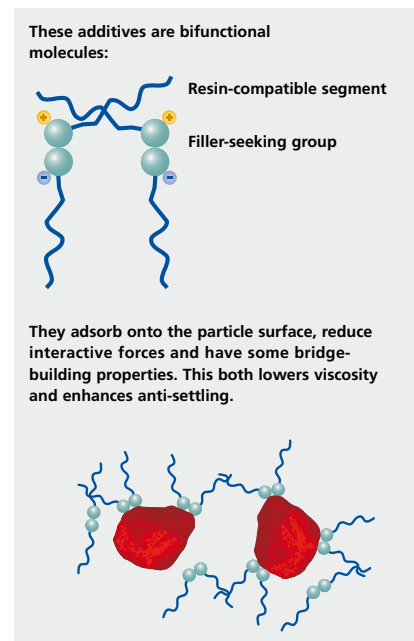


figure 7

### Low Molecular Weight, Polymeric Wetting and Dispersing Additives to Reduce Viscosity and Settling

Wetting and dispersing additives, which function by steric hindrance, are characterized by two special structural features. First, such products contain more pigment/filler affinic groups, i.e. anchor groups or adhesive groups,

that together facilitate a strong, durable adsorption onto the pigment/filler surface. Second, such products contain resin-compatible chains (hydrocarbon entities), which, after adsorption of the additive onto the pigment/filler surface, protrude as far as possible from the pigment/filler surface. This layer of adsorbed additive molecules

with protruding chains is referred to as steric hindrance or "entropic stabilization" (figure 7).

The stabilization is further enhanced by the interaction of the additives' polymeric segments with the resin polymers in such a way that the "envelope", so to speak, around the pigment/filler particles is enlarged. Through specific structural elements composed of pigment/filler affinic groups (polar) and resin-compatible chains (non-polar), these additives exhibit definitive surface-active properties. In other words, they not only stabilize the pigment/filler dispersion, but they also function as wetting additives that lower the viscosity of the filled resin system (figure 8).

### Lower Viscosity, Higher Filler Load

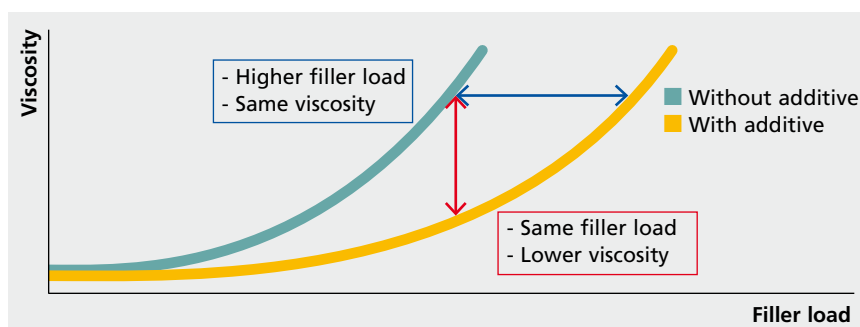


figure 8

### Wetting and Dispersing Additives to Reduce Settling and Improve Color Stability

The controlled flocculation state of fillers and pigments forms three-dimensional wetting structures which facilitate thixotropic flow behavior within the system. The resting state viscosity is rather high as a result of these structures. However, when shear forces are applied, the structures (pigment/filler flocculates) break apart and reduce viscosity. After the shear forces are removed, the flocculates can rebuild. Generally, such systems have a flow threshold. Properties such as sagging and settling can be positively influenced through the above-mentioned rheological behavior. During processing and handling, the shear forces maintain viscosity at a level low enough to ensure easy processability. Then, in the resting state (such as after application), the viscosity increases quickly and provides excellent stability. The high resting state viscosity (in this case, during storage) greatly reduces pigment/filler particle settling speed.

An additional factor should be considered with respect to settling. Often, a small, yet rather hard and compact layer may build up and be resistant to reincorporation. However, in a controlled flocculation system, this does not occur since additive molecules are always between the pigments/fillers. The sedimentation (if it forms at all) is much less compact, has a larger volume, and is therefore easily reincorporated. Controlled flocculation can also control both flooding and floating because the different pigments are bound together in the flocculates and consequently, cannot separate from the mixture.

### Anti-settling and Color Stability BYK-W 940

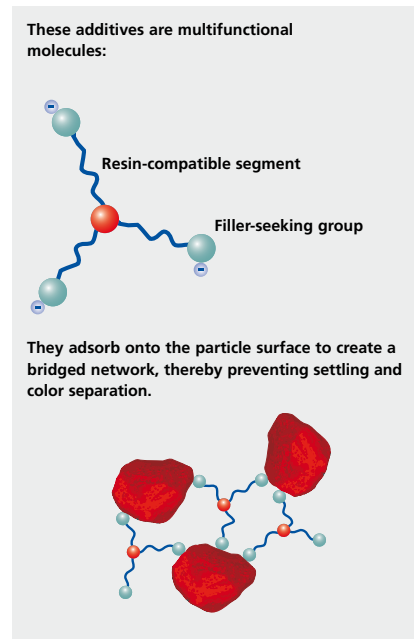


figure 9

### Anti-settling, Better Storage Stability



figure 10

### Wetting and Dispersing Additives for:

	Viscosity Reduction	Viscosity Reduction and Anti-settling	Anti-settling
	– reduced viscosity and dramatically increased filler load	– reduced viscosity and increased filler load – improved storage stability (anti-settling)	– improved storage stability (anti-settling)
Cont. laminating	BYK-W 985		
Putty	BYK-W 969*		
Spray-up, lay-up, casting		BYK-W 966 BYK-W 980	BYK-W 940
Polymer concrete, solid surface	BYK-W 909		BYK-W 940

\* Not recommended for cobalt-promoted systems

figure 11

# Styrene Emission Suppressants

## Straight Paraffin Wax

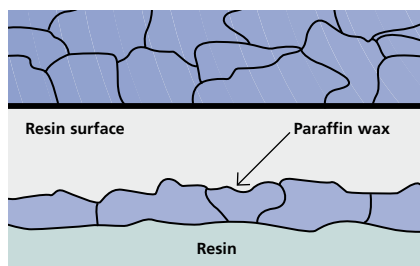


figure 12

## BYK-S 740

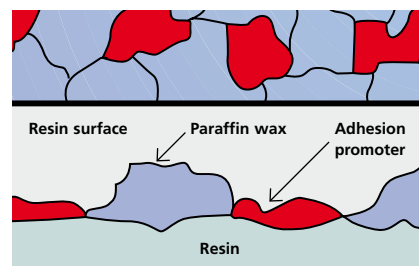


figure 13

## BYK-S 750/BYK-S 760

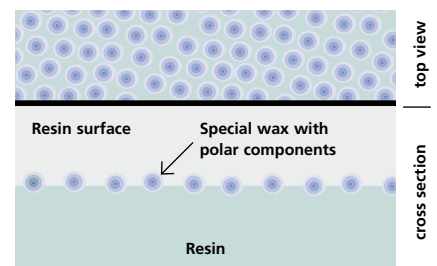


figure 14

FRP fabrication methods utilizing open mold techniques – whether the resin is orthophthalic, isophthalic, DCPD-type, or vinylester – are known to produce

relatively high levels of styrene monomer emissions. Paraffin wax has become one of the most widely used film-forming suppressants to minimize styrene

emissions in open mold applications. Although it suppresses emissions well in orthophthalic resins and less effectively in isophthalics, it is ineffective in vinylesters and DCPD resins.

## BYK-S 740 for Orthophthalic Resins

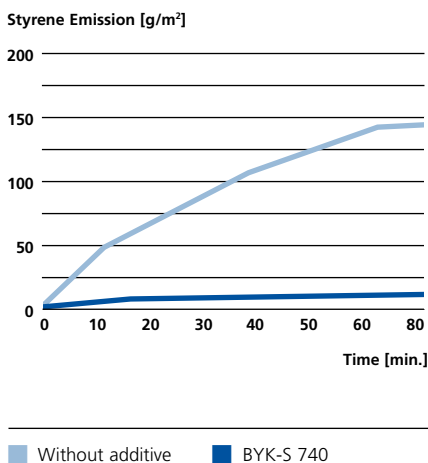


figure 15

Paraffin wax forms a closed film on the surface of orthophthalic and most isophthalic polyester resins. This reduces styrene monomer emissions, but its pure wax nature makes it act as a release film, which does not allow good interlaminar adhesion (figure 12).

**BYK-S 740** combines paraffin wax with a specifically developed adhesion promoter, thereby ensuring good styrene emission reduction with excellent interlaminar adhesion (figure 15).

BYK-S 740 is highly effective in reducing emissions in orthophthalic resins and is also effective in isophthalic polyesters – though to a lesser degree and depending on the resin polarity (figure 13).

## BYK-S 750 for DCPD, Vinylester, and Isophthalic Resins

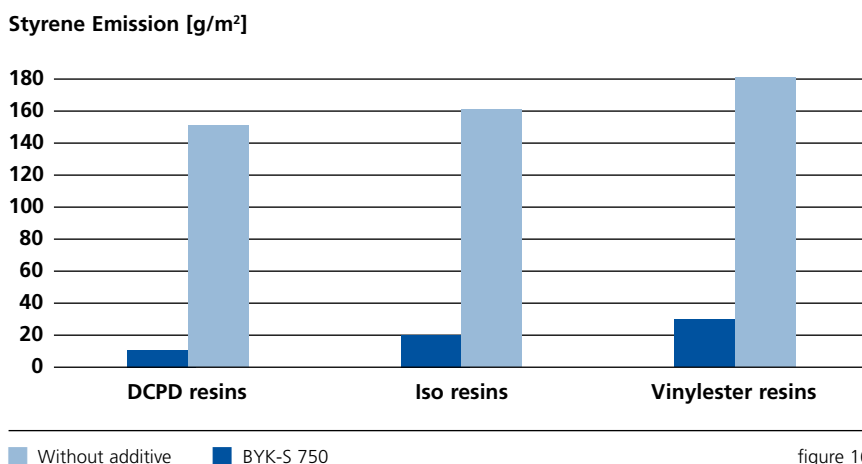


figure 16

Both paraffin wax and BYK-S 740 are too soluble to form a surface film in vinylesters, most DCPD-type resins, and even some isophthalics. BYK-S 750 – developed specifically as a styrene suppressant for DCPD-type resins – forms very fine wax crystals on the resin surface of such DCPD resins. These carry an external polar component, which holds them apart and allows resin from a secondary laminate to penetrate below the wax. The direct contact with the primary laminate is what provides good interlaminar adhesion (figure 14).

**BYK-S 750** is also very effective in vinylester and isophthalic resins (figure 16).

**BYK-S 760** is in terms of performance similar to BYK-S 750 but fulfills food contact regulations. For the current food contact legal status please contact our product safety department or visit [www.byk.com](http://www.byk.com) for further information. Like BYK-S 750, the active substance carries a polar component which holds the wax crystals apart and allows good laminar adhesion. In BYK-S 760, a new technology is used to stabilize the polar component even at higher temperature so that the additive can be melted at 40 °C and processed in liquid form.

### Styrene Suppressants under Practical Conditions

There are various static methods for measuring styrene emission, such as Rule 1162 developed in the United States or the German AVK\* Method. However, these methods do not accurately evaluate the performance of suppressants under dynamic or working conditions. In order to illustrate suppressant performance under such dynamic or working conditions, total emissions during a manual lay-up application were evaluated. However, these values in ppm do not reflect the maximum work place concentrations since such values would actually be lower.

### Application Emission Testing in Manual Lay-up

In this particular test, styrene emissions were measured above the laminate using a Miran infrared detector with its sensor tube placed 15 cm above the horizontal center of the laminate. Air flow was less than 0.1 m/s and an extractor fan was not used. Laminate construction consisted of a three layer mat at 30% by weight with 70 % resin. All resins were MEKP-cured with an average gel time of 40 minutes.

\* German working committee for reinforced plastics

#### DCPD/Orthophthalic Resin (31.5% styrene monomer + 2% alpha-methylstyrene)

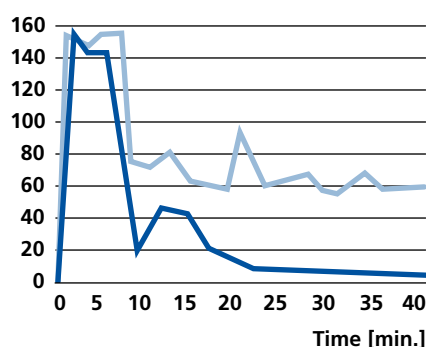
Average styrene monomer emissions are reduced from 78 ppm (sample without additive) to 37 ppm by using 1% BYK-S 750 based on resin weight (see figure 17).

#### Orthophthalic Resin (42% styrene monomer)

Average styrene monomer emissions are reduced from 95 ppm (sample without additive) to 52 ppm by using 1% BYK-S 740 based on resin weight (see figure 18).

### Styrene Emission During Processing

Styrene Emission [ppm] at 20.4 °C



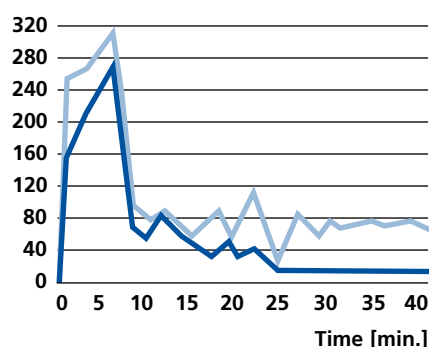
← dynamic → static →

■ DCPD/orthophthalic resin  
■ DCPD/orthophthalic resin with 1% BYK-S 750

figure 17

### Styrene Emission During Processing

Styrene Emission [ppm] at 20.4 °C



← dynamic → static →

■ Orthophthalic resin  
■ Orthophthalic resin with 1% BYK-S 740

figure 18

### Styrene Emission Suppressants

	BYK-S 740	BYK-S 750	BYK-S 760
Orthophthalic resins	0.5–1.0 %		
DCPD-containing resins	–	0.3–1.0 %	0.3–1.0 %
Isophthalic resins	0.5–1.0 %	0.3–1.0 %	0.3–1.0 %
Vinylester resins	–	0.3–1.0 %	0.3–1.0 %
Food contact applications	not recommended	not recommended	0.3–1.0 %

figure 19

### Conclusion:

BYK – LSE – additives reduce styrene emissions by approx. 50%. These additives, though showing limited effectiveness during the dynamic phase, are particularly effective during the static phase.



# Rheology Control Additives

## Why Rheological Additives?

Flow behavior is one of the most important technical properties of a gel coat or laminating resin system. To a great extent, it determines the usability and user-friendliness of the liquid system. The key factor in describing flow behavior is **viscosity**  $\eta$ . However, for most systems, viscosity is not a constant. It depends on a variety of parameters. Besides temperature dependence, the most important parameter from the application standpoint is the **mechanical stress** the liquid system is exposed to. **Rheology** is the interrelationship between viscosity and shear forces, which can be very complex.

The rheology of a liquid system is determined primarily by:

1. the resin (chemistry, molecular weight)
2. the type of thixotrope used
3. the solvent content

Consequently, special rheological additives are required for optimum adjustment of rheological properties. In most cases, these additives are used to improve **sagging** during application; in some cases, they are used to prevent the fumed silica or clay from settling during resin storage. However, the rheological properties described above may also negatively impact the deaeration and surface flow of the liquid system.

## Rheology of Ambient Curing Resins

A major factor, however, is the dependence of viscosity on **shear rate**. For many FRP applications, a relatively large shear range must be taken into account (figure 20). Rather high shear forces ( $>1000 \text{ s}^{-1}$ ) are used to produce these systems (dispersing, blending and filling) as well as during application (rolling, brushing or spraying). However, shear rates are relatively low ( $<1 \text{ s}^{-1}$ ) during storage and in the phase between application and hardening.

## Typical Shear Ranges

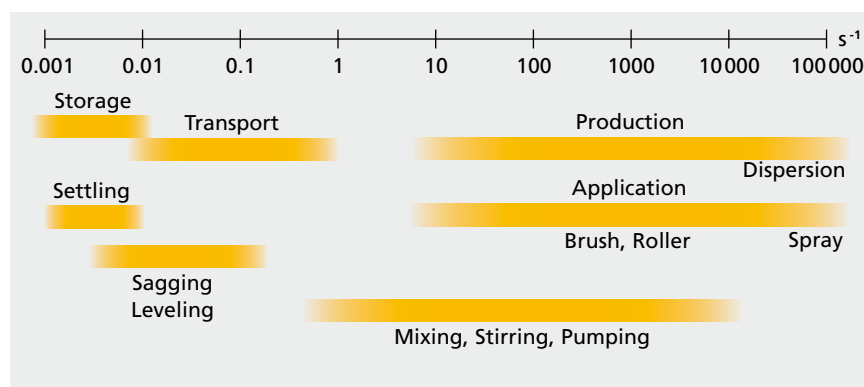


figure 20

## Three-dimensional Network Structures of Solid Thixotropes

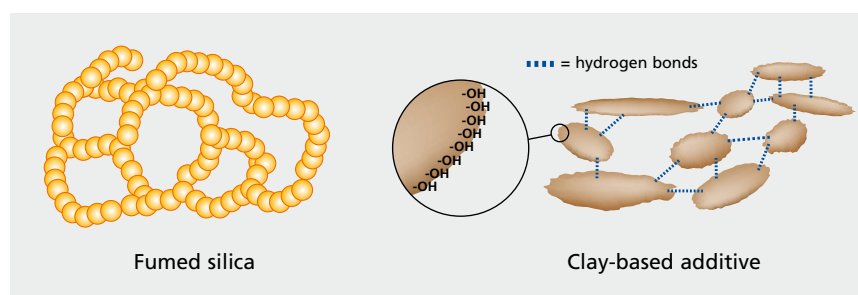


figure 21

A rheological characterization over the entire shear range is best obtained by using rotation viscometers. In all measuring systems of this type, the liquid to be tested is sheared between a stationary surface and a moving surface.

## Solid Thixotropes

Hydrophilic fumed silica and clay-based additives are used as solid thixotropes to control rheology in many UP formulations. The solid thixotrope particles carry hydroxyl groups on their

surface, which by hydrogen bonds are able to create three-dimensional network structures (figure 21). As a result, formulations with solid thixotropes can exhibit pseudoplastic and thixotropic flow behavior.



## GARAMITE

GARAMITE-1985 and GARAMITE-1210 are solid thixotropes based on the patented Mixed Mineral Technology (MMT). These clay-based additives are organically modified in order to meet the polarities of various unsaturated polyester systems. Due to multiple particle morphologies (figure 22) the powder disperses very easily into the resin with only moderate shear force. GARAMITE additives form a network via hydrogen bonds which leads to a pseudoplastic flow behavior (figure 23).

Typically in UPR formulations GARAMITE additives are compared to fumed silica additives on a 1:1 replacement. At equal loading levels, the formulations containing GARAMITE additives exhibit a higher low shear viscosity and a lower high shear viscosity. Therefore a comparison should be set around actual performance parameters such as sag resistance and not based on existing fumed silica rheology profiles.

### Incorporation of GARAMITE Additives into UPR Systems

GARAMITE additives can be added directly to the resin or processed via a pregel, whereas for maximum performance the pregel route should be preferred. Here GARAMITE additives should first be predispersed in monomer or solvent. The following process is highly recommended to ensure maximum performance of GARAMITE additives in all UP resins:

#### Direct addition:

GARAMITE should be added after the addition of air release additives (e.g. BYK-A 555) at low shear forces to the lowest viscosity component of the formula (e.g. monomer). After a mixing period at moderate shear force, all the other components of the formulation should be added.

#### Pregel:

Add GARAMITE additives to the monomer phase. If necessary an air release additive can be added prior to the GARAMITE additive. Typically, a standard high speed mixer is sufficient for mixing

GARAMITE additives. The mixer speed should be sufficient to generate and maintain a visually apparent vortex for 5 to 10 minutes. Additional shear may entrain air into the pregel. For maximum efficiency, the concentration of GARAMITE additive in the pregel should be above 8 % and not exceed 15 %. At these concentrations, the GARAMITE additive pregel will remain pumpable and pourable. The GARAMITE additive pregel may be added to the formulation at any point in the manufacturing process. In some instances it is preferable to drop the resin into the GARAMITE additive pregel.

### Mixed Mineral Technology (MMT)

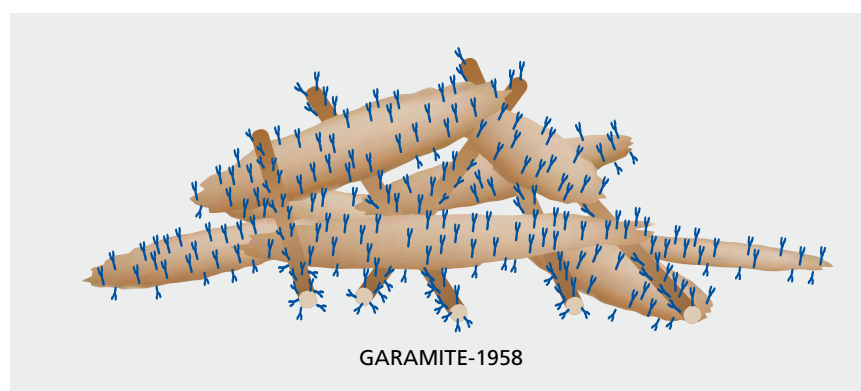


figure 22

### GARAMITE-1958 vs. Fumed Silica

#### Viscosity (Pa-s)

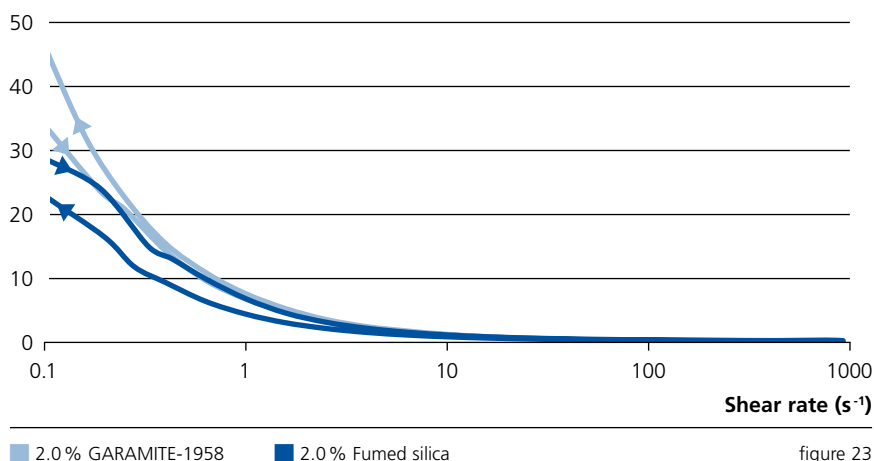


figure 23

In both cases do not add any dispersant, wetting agent, surfactant or rheology booster prior to the addition and mixing of GARAMITE additives into the monomer or solvent.

The overall advantages of using GARAMITE compared to other solid thixotropes are:

- only minimal shear is necessary for incorporation
- standard production dissolver are sufficient for incorporation
- reductions in processing time of 50 % or more are common
- high shear forces are not required
- heat activation is not required
- polar activation is not required
- less dust is produced

#### BYK-R 605, the Thixotropy Booster

The rheological additive BYK-R 605 can best be described as thixotropy booster. If BYK-R 605 is used in combination with a solid thixotrope (fumed silica or clay), the additive acts on the solid particles as a wetting additive and as a dispersing additive which flocculates in a controlled manner. The additive has free OH groups, which allow hydrogen bonding between the hydroxyl groups. Structures form with a distinctively closer mesh, and the thixotropy is increased as a result (figure 24).

#### Intensification of the Network Structure with BYK-R 605

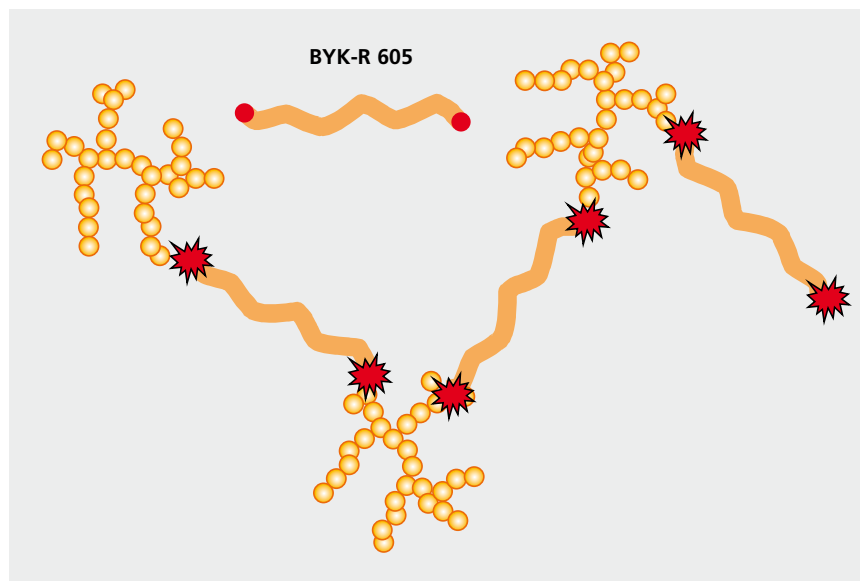


figure 24

### Where is BYK-R 605 Used?

BYK-R 605 stabilizes and increases thixotropic flow behavior of formulations containing fumed silica and clay. It also facilitates incorporation of fumed silica into the resin system. This last aspect is particularly apparent in laminating resins, as the shear forces normally available here for incorporation are lower than in gel coats. In combination with GARAMITE-1958, the thixotropy booster BYK-R 605 is able to increase the viscosity and in addition, to move the rheological profile of the system from pseudoplastic to thixotropic, which is beneficial in terms of air release, flow, and leveling. (figure 25).

It is also possible to replace some of the fumed silica or clay with BYK-R 605 to minimize the silica's effect on transparency while maintaining the thixotropy. BYK-R 605 can as well be used to reduce the content of solid thixotropes in the final formulation without losing rheological performance, but gaining production speed and lower formulation costs (figure 26).

### GARAMITE-1958 vs. Fumed Silica in Combination with BYK-R 605

Viscosity (Pa-s)

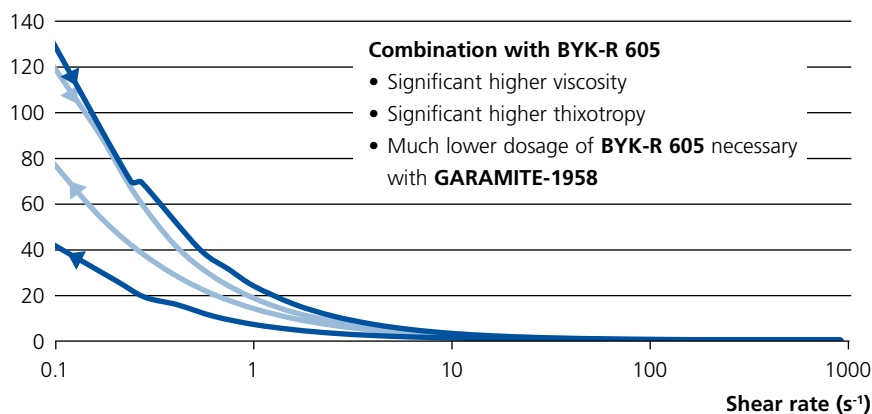


figure 25

### Less Amount, Same Result

Viscosity (Pa-s)

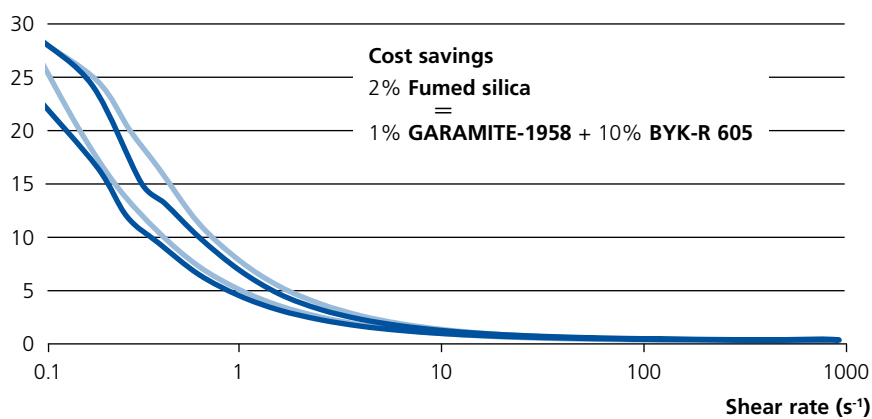


figure 26

The effectiveness of BYK-R 605 is shown in Figures 27 and 28 in combination with fumed silica and GARAMITE-1958. Generally, BYK-R 605 can be used in all types of ambient curing resin systems. In vinylester resins, it is even possible to use hydrophilic fumed silica when combined with BYK-R 605 (figure 29) and still obtain optimal thixotropy effects. BYK-R 605 shows no effect on gel time or cure in orthophthalic-, iso-, or iso-NPG, and DCPD or DCPD blends.

Laminating Resin with Fumed Silica

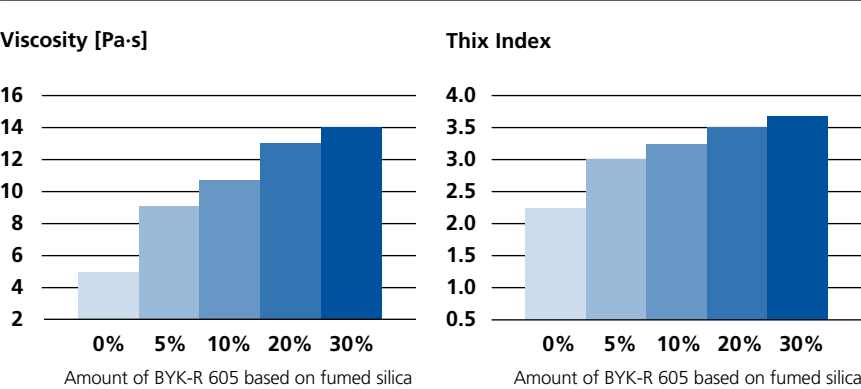


figure 27

Laminating Resin with GARAMITE-1958

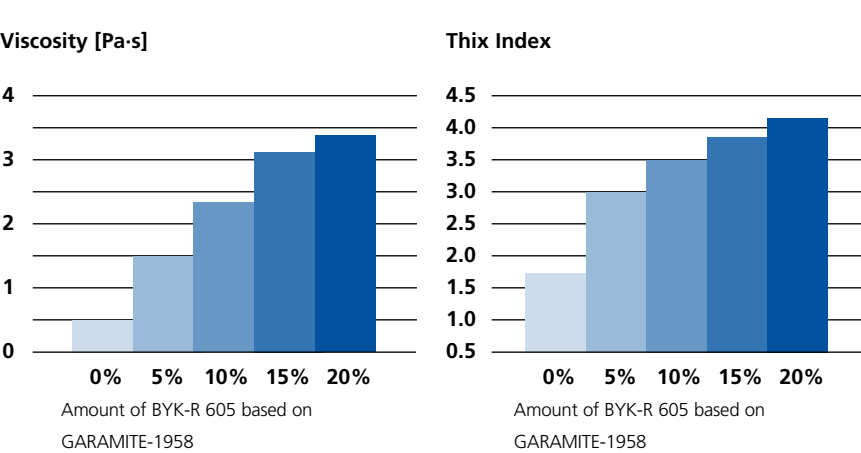


figure 28

Vinylester Gel Coat

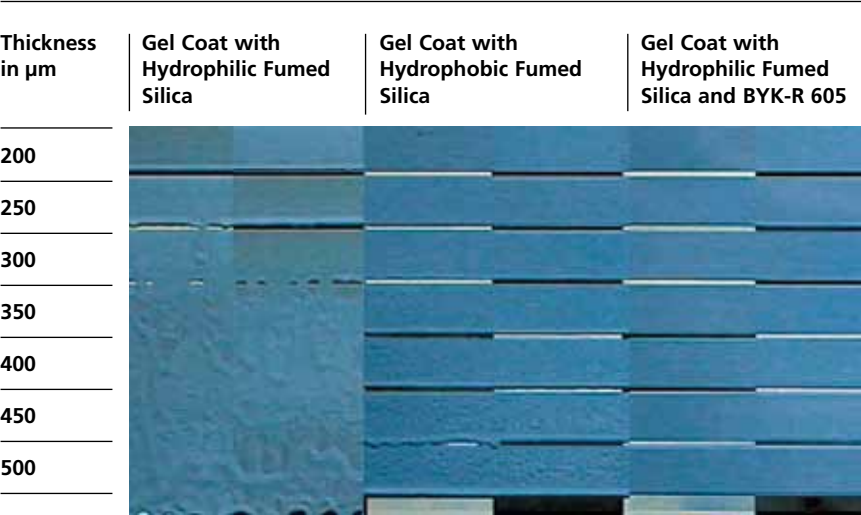


figure 29

## Processing Additive to Prevent Foaming in Vinylester Resins

Vinylesters are used whenever high corrosion resistance is required; pipes and containers are thus typical applications. Since the use of standard curing agents such as methyl ethyl ketone peroxide (MEKP) is always difficult with vinylesters, other curing agents such as CHP, cumyl hydroperoxide, have been used.

With **BYK-P 9928**, curing standard vinylesters with standard curing agents such as MEKP is now possible (figure 30).

The vinylester's structure has an impact on the cobalt complex and therefore, on the activity of the cobalt in the resin. BYK-P 9928 interferes with the interaction between the cobalt and the resin so that the cobalt is less reactive.

### Foam Generation in a Vinylester Resin System



Without additive

With BYK-P 9928

Curing agent: MEKP

figure 30

BYK-P 9928 changes the activity of the cobalt accelerator by changing the cobalt complex which is indicated by a color change (figure 31). The additive therefore has a direct influence on the curing process so that gel time and peak exotherm can be influenced.

To check the influence on the curing, we recommend starting with a dosage of 1% on resin. If there is an effect on foaming, the dosage can be reduced until the effect disappears. At that point, the optimum dosage has been determined. Curing, gel time, and peak have to be checked and, if necessary, adjusted.

### Color Change with BYK-P 9928



Without additive

With BYK-P 9928

figure 31

BYK-P 9928 has been tested with respect to chemical resistance of thermosetting resins used in glass fiber reinforced structures according to ASTM C581-03 (2008). The additive has no negative effect on the resistance towards pure water, hydrochloric acid (10%), toluene, isobutanol, or sodium chloride (saturated, 50%) in the test system.

Preventing gas formation during curing leads to less entrapped air in the laminate so that higher resistances are possible, especially in hot water boiling tests (figure 32). In infusion systems, this effect ensures the success of the infusion process.

BYK-P 9928 is not an air release agent. It has no influence on mechanically incorporated air. Combining BYK-P 9928 with an air release additive creates a synergy effect (figure 33).

Glass Fiber Reinforced Laminate



figure 32

BYK-P 9928 vs. Air Release Additives

Effect on	BYK-P 9928	Air Release Additive e.g., BYK-A 515
Mechanical air e.g., during production and/or application	No	Yes
Reaction air e.g., oxygen formation	Yes	No

figure 33

## Summary of Additive Recommendations

### Additive Recommendations for Ambient Curing Polyester Resins

		First Recommendation	Second Recommendation
<b>Lay up/spray up</b>	Air release	<b>BYK-A 515</b> <b>BYK-A 555</b> <b>BYK-A 560</b>	BYK-A 501
	Viscosity reduction	<b>BYK-W 966</b>	
	Rheology	<b>BYK-R 605</b> <b>GARAMITE-1958</b>	GARAMITE-1210
	Prevention of chemical foam in vinylester resins	<b>BYK-P 9928</b>	
	Styrene emission	<b>BYK-S 740</b> <b>BYK-S 750</b>	BYK-S 760
<b>Filament winding</b>	Air release	<b>BYK-A 560</b>	BYK-A 515
	Mechanical properties	<b>BYK-C 8000</b>	
	Wetting	<b>BYK-330</b>	BYK-370
<b>Casting, polymer concrete, solid surface</b>	Air release	<b>BYK-A 555</b>	BYK-A 515
	Viscosity reduction	<b>BYK-W 909</b>	BYK-W 985
	Mechanical properties	<b>BYK-C 8000</b>	BYK-C 8002
	Prevention of chemical foam in vinylester resins	<b>BYK-P 9928</b>	
<b>Transparent</b>	Air release	<b>BYK-A 550</b>	BYK-A 500
<b>Continuous laminating</b>	Air release	<b>BYK-A 560</b>	BYK-A 555
	Flow/leveling, anti-cratering	<b>BYK-330</b> <b>BYK-378</b>	BYK-358 N
<b>Infusion/RTM</b>	Air release	<b>BYK-A 560</b>	BYK-A 525
	Wetting	<b>BYK-330</b>	
	Viscosity reduction	<b>BYK-9076</b>	BYK-9077
	Prevention of chemical foam in vinylester resins	<b>BYK-P 9928</b>	
<b>Green resins</b>	Air release	<b>BYK-A 505</b>	
	Styrene emission	<b>BYK-S 760</b>	

figure 34



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