

APPLICATION INFORMATION ADDITIVES FOR AMBIENT CURING POLYESTER RESINS

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Ambient curing unsaturated polyester and vinylester resins

Unsaturated polyester resins are usually a solution of a polyester with reactive double bonds in an equally reactive monomer, usually styrene. These resins mentioned in this brochure are cured at room or slightly elevated temperature with the aid of a accelerator and a peroxide to form a thermoset material. Vinyl ester resins are chemically more like epoxy resins, but in their present form they also have reactive double bonds, are dissolved in styrene, and behave similarly to "true" UP resins with respect to application and curing.

Unsaturated polyester resins and vinyl ester resins, due to good commercial availability and competitive cost, are used in a wide variety of different processes for equally diverse applications, each of which must meet its own unique requirements, e.g. FRP boat hulls, various types of pipes, buttons, putties, wind blades, drainage systems, automotive and truck parts, sinks, etc.

This brochure summarizes our additive recommendation for these systems and applications.

For additional information on additives and technical topics, please contact us: **Thermosets.BYK@altana.com**

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Note

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).

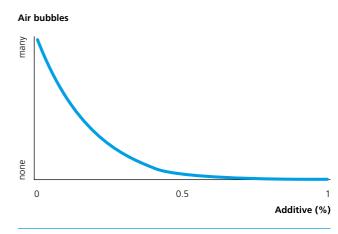
3. Bubbles burst on the surface

Bubble-stabilizing substances are displaced, and the bubbles burst.

Optimized dosage

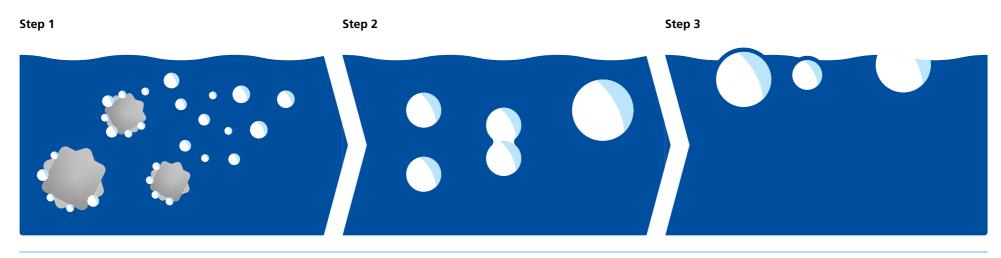
BYK air release additives achieve excellent deaeration even at small dosage levels.

BYK air release additives



G. 02

Air release additives work in three steps



Product recommendations

Product	Remarks
BYK-081	is a very efficient defoamer with only slight haziness and has food-contact approval. Recommended for vinylester resins.
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.
	Т.01

Selection chart air release additives



Deaeration of an unsaturated polyester

Without additive

With additive



Test method

The test method shown in figure G.05 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.

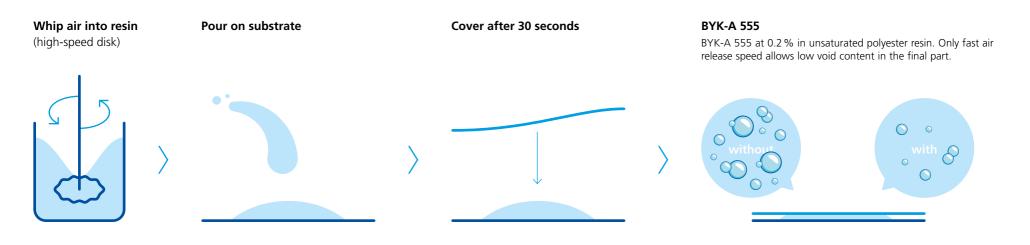
Immediately after agitation, pour the resin on a surface. Allow 30 seconds deaeration time, then cover with Mylar film.

After casting is completely cured, visually evaluate the air release additive effect.

Application areas

Product	UP resins	Vinylester resins	Fiber wetting properties	Gel coats	Casting	Transparent parts
BYK-081	•	•		0	•	•
BYK-A 500	0			0	0	•
BYK-A 501	0			0	0	
BYK-A 505	•				0	
BYK-A 515	•	•	•	•	•	
BYK-A 550	0			0	•	•
BYK-A 555	•			•	•	
BYK-A 560	•		•	0	0	
Excellent O	Good					

Test principle to evaluate air release





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 (G.06).

BYK-W 908, BYK-W 909*, BYK-W 969, BYK-W 985

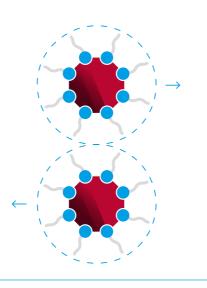
These additives are monofunctional molecules:



Filler-seeking group

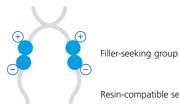
Resin-compatible segment

They adsorb onto the particle surface and reduce interactive forces, which lowers viscosity.



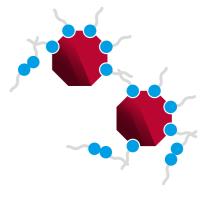
Viscosity reduction and anti-settling: BYK-W 980, BYK-W 966

These additives are bifunctional molecules:



Resin-compatible segment

They adsorb onto the particle surface, reduce interactive forces, and have some bridgebuilding properties. This both lowers viscosity and enhances anti-settling.



Low molecular weight, polymeric wetting and dispersing additives to reduce viscosity and settling

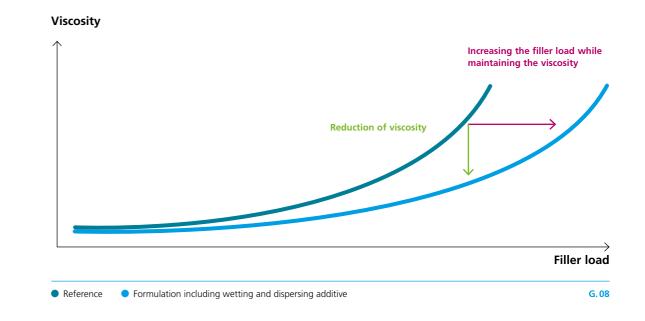
Wetting and dispersing additives, which function by steric hindrance, are characterized by two special structural features. First, such products contain more pigment/filler affinic groups, i.e. anchor groups or adhesive groups, that together facilitate a strong, durable adsorption onto the pigment/filler surface. Second, such products contain resincompatible chains (hydrocarbon entities), which, after adsorption of the additive onto the pigment/filler surface, protrude as far as possible from the pigment/filler into the surrounding resin solution.

This layer of adsorbed additive molecules with protruding chains is referred to as steric hindrance or "entropic stabilization" (G.07).

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 (G.08).

Application example for wetting and dispering additives



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.

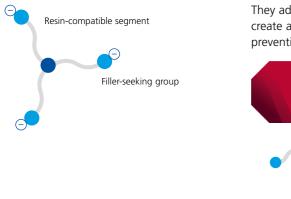
Anti-settling, better storage stability



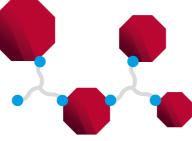
G. 09

Anti-settling and color stability BYK-W 940

These additives are multifunctional molecules:



They adsorb onto the particle surface to create a bridged network, thereby preventing settling and color separation.



Wetting and dispersing additives for:

Application	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 985 BYK-W 908/BYK-W 909**		BYK-W 940		

Styrene emission suppressants

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.

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 (G. 11).

BYK-S 740*/BYK-S 740 N combines paraffin wax with a specifically developed adhesion promoter, thereby ensuring good styrene emission reduction with excellent interlaminar adhesion (G. 14).

BYK-S 740*/BYK-S 740 N 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 (G. 12).

Both paraffin wax and BYK-S 740 N are too soluble to form a surface film in vinylesters, most DCPD-type resins, and even some isophthalics. BYK-S 750 N - 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 (G. 13).

BYK-S 750 N is also very effective in vinylester and isophthalic resins (G. 15).

BYK-S 750 N/BYK-S 760

+

Straight paraffin wax



Resin

G.11

BYK-S 740*/BYK-S 740 N

Adhesion promoter

Resin

(+)

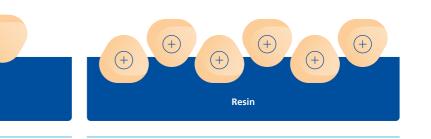
(+)

Special wax with polar components

(+)

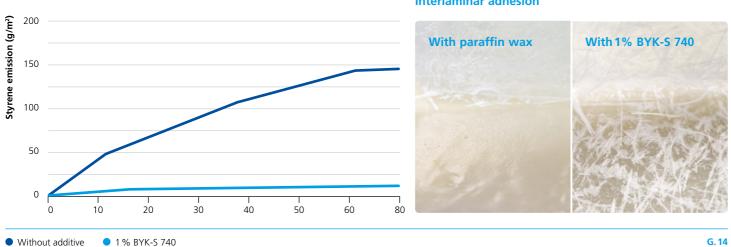
(+)

G.13

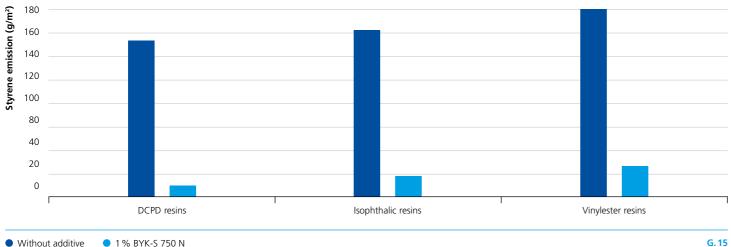


G.12

BYK-S 740*/BYK-S 740 N for orthophthalic resins



BYK-S 750 N for DCPD, vinylester, and isophthalic resins



• Without additive • 1 % BYK-S 750 N



Q

*Not available in EU

BYK-S 760 is, in terms of performance, similar to BYK-S 750 N, but fulfills food contact regulations. For the current food contact legal status, please contact our product safety department or visit www.byk.com for further information. Like BYK-S 750 N, 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 temperatures, so that the additive can be melted at 40 °C and processed in liquid form.

Styrene emission suppressants

Application	BYK-S 740*/BYK-S 740 N	BYK-S 750 N	ВҮК-S 760
Orthophthalic resins	0.5–1.0%	_	0.3–1.0 %
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 %

* Not available in EU

** For details on food contact use, please refer to the food contact sheet available on www.byk.com/en/service/regulatory-affairs/food-contact.

Key benefit

BYK – LSE – additives can reduce styrene emissions by more than 80%. These additives, though showing limited effectiveness during the dynamic phase, are particularly effective during the static phase.

$\equiv \Diamond$

Rheology control additives

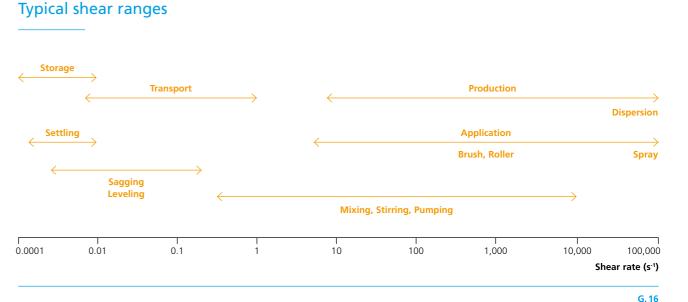
Why rheological additives?

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. 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.



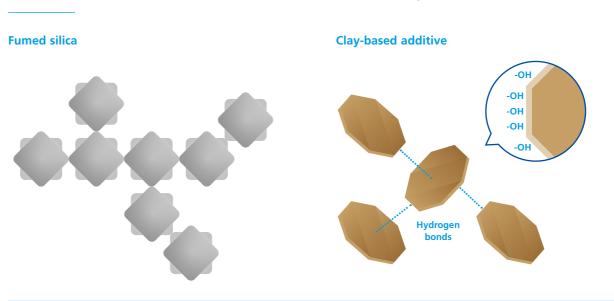
Rheology of ambient curing resins

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 (G. 16). Rather high shear forces (>1000 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 s⁻¹) during storage and in the phase between application and hardening.

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 (G. 17). As a result, formulations with solid thixotropes can exhibit pseudoplastic and thixotropic flow behavior.



Three-dimensional network structures of solid thixotropes

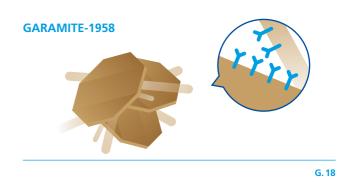
G. 17

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 (G. 18), 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 (G. 19).

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.

Mixed mineral technology (MMT)



GARAMITE-1958 vs. fumed silica

Improved bulk density of GARAMITE-1958

/iscosity (mPa*s) Good sag resistance GARAMITE Easy wet out Fumed silica 10 100 Shear rate (s-1)

Fumed silica

GARAMITE-1958



15 g in 150 ml flask each

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 mixer is sufficient for mixing GARAMITE additives. No high shear force is needed. 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. 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:

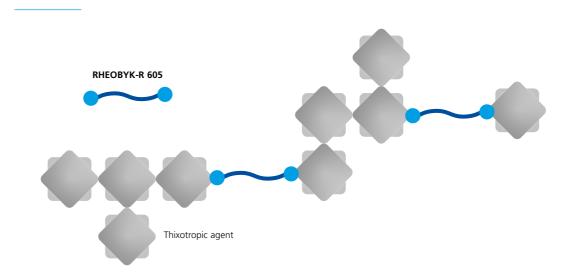
- only minimal shear is necessary for incorporation
- standard production dissolver are sufficient for incorporation
- reductions in processing time of 50 % or more are common
- high shear forces are not required
- heat activation is not required
- polar activation is not required
- less dust is produced



RHEOBYK-R 605, the thixotropy booster

The rheological additive RHEOBYK-R 605 can best be described as thixotropy booster. If RHEOBYK-R 605 is used in combination with a solid thixotrope (hydrophilic 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 (G.21).

Intensification of the network structure with RHEOBYK-R 605





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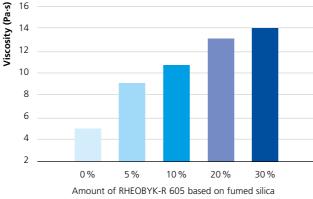
Where is RHEOBYK-R 605 used?

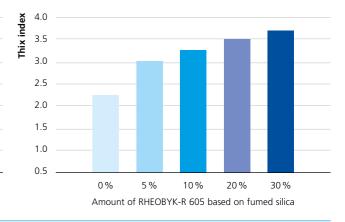
RHEOBYK-R 605 stabilizes and increases thixotropic flow behavior of formulations containing fumed silica and clay. It also facilitates incorporation of fumed silica into the resin system. This last aspect is particularly apparent in laminating resins, as the shear forces normally available here for incorporation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

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

The effectiveness of RHEOBYK-R 605 is shown in G. 22 and G. 23 in combination with fumed silica and GARAMITE-1958. Generally, RHEOBYK-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 RHEOBYK-R 605 (G. 24) and still obtain optimal thixotropy effects.

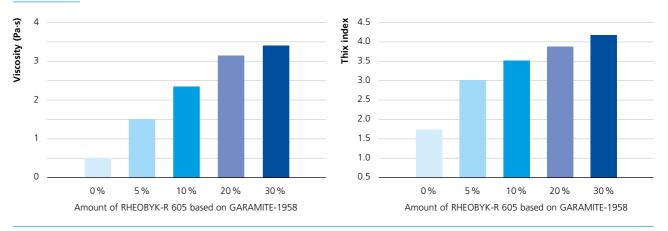
Laminating resin with fumed silica





G.22

Laminating resin with GARAMITE-1958



Vinylester gel coat

Thickness in μm	Gel coat with hydrophilic fumed silica	Gel coat with hydrophobic fumed silica	Gel coat with hydrophilic fumed silica and RHEOBYK-R 605
50			
100			
150			
200	man		
250	win and		
300			
350			
400			
450			
500			

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 (G.25).

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.

BYK-P 9928 changes the activity of the cobalt accelerator by changing the cobalt complex, which is indicated by a color change. 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. Foam generation in a vinylester resin system

Without additive

With BYK-P 9928



Curing agent: MEKP

 $\equiv Q$

BYK-P 9928 has been tested with respect to the 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 (G. 26). 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 (T.04).

Glass fiber reinforced laminate



G.26

BYK-P 9928 vs. air release additives

Effect on	ВҮК-Р 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

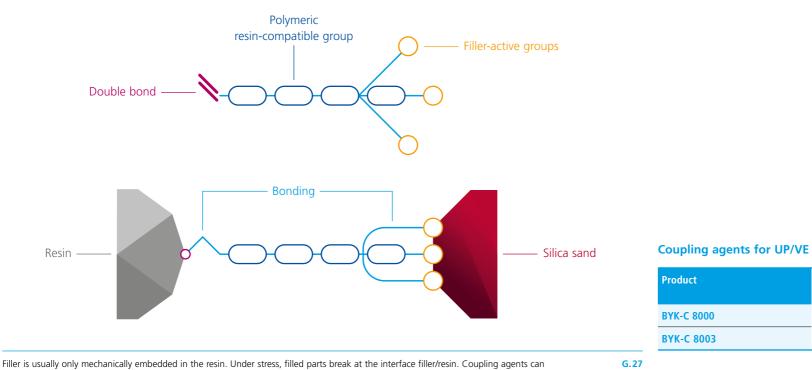
T. 05

Coupling agents

Coupling agents are used to improve the bonding of fibers and fillers to the polymer matrix. Most coupling agents therefore consist of two reactive groups, one bonding to the surface of the fiber or filler, and the other bonding to the matrix during polymerization. This significantly improves a number of properties.

The use of coupling agents, for example, results in higher mechanical load capacities, an improvement in chemical resistance, or an increase in UV stability.

Mode of action



Product	Filler/fiber
BYK-C 8000	Sand, quartz, glass beads
ВҮК-С 8003	Glass fibers

strengthen the interface between filler and resin by forming bonds, resulting in a remarkable improvement of mechanical properties.

Summary of additive recommendations

Additive recommendations for ambient curing polyester resins

Application	Air release	Anti-sedimentation of fumed silica	Flow/leveling, anti-cratering	Mechanical properties	Prevention of chemical foam in vinylester resins	Rheology	Styrene emission	Substrate wetting	Viscosity reduction
Lay up/spray up	BYK-A 515 ● BYK-A 555 ● BYK-A 560 ● BYK-A 501 ○	ANTI-TERRA-210 •			ВҮК-Р 9928 ●	RHEOBYK-R 605 • GARAMITE-1958 • GARAMITE-1210 O	BYK-S 740*/BYK-S 740 N ● BYK-S 760 ● BYK-S 750 N ○		BYK-W 966 🗢
Filament winding	BYK-A 560 ● BYK-A 515 〇			BYK-C 8003 ●				BYK-330 ● BYK-370 ○	
Casting, polymer concrete, solid surface	ВҮК-А 555 ● ВҮК-А 515 〇			BYK-C 8000 •	BYK-P 9928 ●	_			BYK-W 908 ● BYK-W 985 ● BYK-W 909* ○
Transparent	BYK-081 ● BYK-A 550 ● BYK-A 500 ○								
Continuous laminating	ВҮК-А 560 О ВҮК-А 555 О		BYK-330 ● BYK-378 ● BYK-361 N ○						
Infusion/RTM	BYK-A 560 ● BYK-A 515 ○			BYK-C 8003 (glass fiber) 🔵	BYK-P 9928 ●			ВҮК-330 🔵	BYK-W 985 ● BYK-W 908 ○
Green resins	BYK-A 505 🔵						BYK-S 760 •		



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