Additives for the Closed Mold Application
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Applications

Within the Closed Mold Application we target resin – filler – glass based material during production and processing. As these mixtures are used in compound production and pultrusion, we want to describe the additives in one brochure, which cover all these applications.

Molding Compounds (SMC, BMC and TMC) are fiber-reinforced materials, which primarily consist of a thermosetting resin, glass fibers reinforcement and filler. Additional ingredients such as low profile/shrink additives, cure initiators, thickeners, and mold release agents are added to enhance performance and/or processing of the material. The organic content is less than 30 per cent by weight, usually an unsaturated polyester resin, which cures by means of a cross-linking reaction. Fiberglass reinforcement guarantees superior mechanical properties.

Glass fibers in SMC (Sheet Molding Compound) are chopped into length of 25 or 50 mm. The amount can vary from 20 to 60 per cent by weight. In BMC (Bulk Molding Compound) shorter fibers (6-12 mm) and lower dosage, 10-18 per cent are used. In TMC (Thick Molding Compound) fibers from (12-25 mm) at a level of 10-20 per cent are used.

SMC, BMC and TMC are compounds, which are further processed in either compression, or injection molding at elevated temperatures (130-170 °C).

Pultrusion is an automated manufacturing process for the production of constant cross-sectionally shaped profiles of fiber-reinforced composites. The polymer reinforced matrix can be formulated to meet the most demanding chemical, flame retardant, electrical and environmental conditions. The reinforcements of the pultruded matrix are usually glass fiber rovings or woven fabrics. Sometimes non-woven mats are used as cross sectional reinforcements or as outside protective layers. The total amount of the reinforcement is in the range of 50-80%.
One of the most important steps in the production of compounds is the homogeneous distribution of solid particles (fillers) within the resin system. If this particle-grinding step is not optimized, a wide variety of defects may occur.

Agglomerates are reduced in size during the dispersion phase; ideally this leads to the production of primary particles. Agglomerates represent particle “groupings” where the interstitial spaces between the individual particles contain air and moisture. These individual particles contact each other along their edges and corners. Interactive forces between the particles are relatively small so they can be separated with traditional dispersing equipment. (In contrast, aggregates are more compact and exhibit planar contact between the individual particles and are much more difficult to separate into primary particles.)

**Working Mechanism**

In the dispersion phase (figure 4), energy is added to the system and therefore smaller particles (with greater surface area) are formed. The system then endeavors to escape this energy rich state and return to its previous low energy condition. This is evidenced by the finely distributed fillers coming back together to form flocculates. From a structural view, flocculates are similar to agglomerates; the interstitial spaces between flocculates are filled with resin solution rather than air.

The various processes which occur during grinding can be divided into the following three steps (figure 5).

**Step 1** represents the true filler grinding stage. Through mechanical energy (impact and shear), the filler agglomerates are separated.

In the concluding **Step 3**, the filler dispersion must be stabilized in order to prevent the formation of uncontrolled flocculates. Special techniques make it possible to keep the filler particles at appropriate distances from one another so that they do not flocculate. In most applications stabilization of the deflocculated state is desirable. Steps 1 (wetting) and 3 (stabilization) are influenced by additives. Wetting additives accelerate the wetting of filler agglomerates by the resin, and dispersing additives stabilize the dispersed filler.
Deflocculation generates a rather Newtonian flow behavior along with reduced viscosity. In this manner, flow behavior is improved and a higher filler loading is possible. The structure of the classical deflocculating additives is based on one or more spatially close filler affinic groups and a number of resin-like chain structures. Such additives are low molecular weight polymers that adsorb upon the filler surface and stabilize the deflocculated condition by steric hindrance.

**Practical Hints and Suggestions**

**Recommended use levels:** The proper use levels of wetting and dispersing additives, as with all additives, is of prime importance. Since the additive is designed to attach to the filler surface, the required dose of additive depends upon the available filler surface.

**Point of addition:** Wetting and dispersing additives should be incorporated first into the resin to achieve optimum performance. The formulation and the order of addition of the individual components can influence dispersion quality.

**Side-effects:** Two primary reasons for using wetting and dispersing additives are (1) the wetting of filler and (2) the stabilization of the filler dispersions. Sometimes rheological effects such as increasing resistance for settling are found. It is important to realize that alteration of rheological properties may influence the flow behavior.

**Pigmentation of the Compounds**

An essential step in the production of compounds is the incorporation of pigments into the paste. In this stage, small particle pigment powders, which generally come in the form of agglomerates, must be dispersed homogeneously in the liquid phase of the paste. The wide range of BYK wetting and dispersing additives can help to obtain perfect color of the compound.

Pigment pastes (pigment concentrates) have found a wide range of applications in the processing of compounds. They contain up to 70% pigment loading and are used for tinting or as the basis for complete color batches. Without additives, it would be extremely difficult to obtain such a high amount of pigment. BYK additives stabilize these pastes and ensure their easy handling and processing.

(See brochure “Additives for Pigment Concentrates”, L-TI 1).
Special liquid processing additives are used for two reasons. On one hand they improve the properties of the produced part. On the other hand they stabilize viscosity and homogeneity of the compound. They also improve the flow behavior, which usually means easier filling of the mold.

**Pigmented Low Shrink Application**

The phenomenon of non-homogeneous pigmented low shrink parts after molding is a well-known, non-desired challenge for low shrink formulations. Whereas anti-separation additives prevent the fast phase separation of polystyrene or polymethyl-methacrylate from the unsaturated polyester resin, effects shown in the figure 8 are polarity, loading and flow related phenomena that still occur even when using an anti-separation additive. These effects are not always visible in the compound but usually stronger in the final part. The processing additives replace the classic stearates that are the main cause for many of the defects in pigmented compounds. Therefore the processing additives also need to have excellent mold release properties to enable the molder to release the parts from the tool. Grey formulations that are often used in the electrical industry can be stabilized enormously and will result in very homogeneous pigmented parts. Figure 9 shows examples of grey parts with and without processing additive. In the area of flame retardant formulations where aluminum trihydrate is used as flame retardant filler, the pigmentation is even more critical.

As the additive absorbs on the filler, the paste and the compound are stabilized extremely well and no separation occurs. By using processing additives high filled systems flow much better than when no processing additive is used. This results in smoother surfaces. This can clearly been seen on larger molded parts were the light reflection has improved (figure 10). Other effects like the water absorption of the molded part are not influenced. The parts with processing additive show improved weather-ability usually due to the fact that the surface is more closed and much smoother.
LP CLASS A

High performance Class A SMC formulations can become sensitive when changes are implemented. Not only the molding quality but also bonding and painting can be influenced. A replacement of certain formulation components is not always recognized as the obvious way for the optimization. Using the processing additive for LP Class A systems will result in direct improvements like a better and more homogeneous flow of the compound with good mold release properties, a positive influence on the emission for inner parts, a better wetted surface for painting and bounding, better paint adhesion and less sensitivity to the placement and size of the cut SMC in the mold were observed.

To highlight some results:

• Low emission and smell are one of the most important demands for use of parts inside the car. Every component of the formulation, which has a negative impact on the emission, will eventually come under fire. All materials have to be stable and must not contribute to either emission or smell. By using the processing additive we find a positive influence, ⇒ less emission and no contribution to the smell.

• Wetting of the molded part depends primarily upon the surface tension of the liquid and the critical surface tension of the surface to be wetted. As a general rule, the surface tension of the liquid must be lower than or at least equal to the surface tension of the substrate. Improper wetting is to be expected when the surface tension of the liquid is higher than the surface tension of the substrate. To demonstrate the effect, contact angle measurements can be illustrative (figure 11). Equilibrium geometry of the liquid drop shows the interactions between the surface and the liquid. Measured contact angles can then be used in conjunction with theories published in scientific literature to determine the surface free energy of a solid, characterizing solid surfaces regarding wettability or adhesion properties.

• Bonding tests and paint tests show also real improvements.

• For Class A parts, painting is very important. In many cases, In Mold Coating is used to prevent paint defects afterwards. Due to the chemistry of this processing additive, we could improve the IMC distribution and bonding. Paint studies were performed in several industrial programs. With a Gravelometer we checked the adhesion. Also here we got very good results.

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Droplet Shape on Molded Plates

![Control formulation](image1.png) ![Formulation with processing additive](image2.png)

figure 11
Processing Additives

Surface Smoothness

Long-term Waviness

- With the processing additives we have a big influence on the flow of the compound in the mold and the appearance of the molded part. Evaluation of the moldings with, for example, Diffracto will show this effect. A whole series of tests were performed to obtain more data regarding the relationship between the waviness of the molded part and its dependence on charge size and placement in the mold. Pictures were taken from the Diffracto screen during the evaluation of Long Term waviness (figure 12).

Processing Additives for Headlamps

- Complex structures of the headlamps require a better material that is able to fill all details of the cavity and achieve a perfectly molded part with excellent surface.
- Smaller dimensions cause higher temperatures in the headlamp.
- Polycarbonate covers, as compared to glass, causes less heat exchange due to lower thermal conductivity of polycarbonate.
- Encapsulation of the headlamps causes less cooling at the backside of the headlamp, as well.

Higher temperatures cause sublimation of several components, like the typically used release agent, out of headlamps. This will be seen as a haze on the cold parts in a headlamp, called fogging. To prevent fogging, new formulations have been developed with the appropriate processing additive. The processing additives were specially designed for many different types of resin systems but also for incompatible resin systems such as UP/PS or UP/PMMA. They compatibilize the resin system with the other ingredients such as fillers, pigments, monomer-free resin from the pigment pastes and the fibers. In some cases the incompatibility of the resin system is so high that in addition to the processing additive, the use of an anti-separation additive is still necessary.
Working Mechanism
On a practical point of view, the production of the compound should be: a very easy distribution of all the raw materials during mixing. Liquids, like our processing additives are easy to homogenize. Processing additives are multifunctional surface active materials, which prevent adhesion of a compound to the surface of a tool. They also build up a yield point (figure 16), which keeps the compound stable after mixing. In other words: this means the viscosity is increasing after mixing (thixotropy), but is reversible under stirring. Reversible bonding becomes disrupted under molding or injection pressure. The additive moves to the surface as a result of its incompatibility with the resin. Also during flow, the surface active part of the additive goes to the surface and prevents adhesion of compound to the tool surface. But after closing the mold, before curing starts, orientation takes place again.

Due to this characteristic of the additive, no residue is left on the tool surface (figure 17). Processing additives improve flow in the mold and make it easier to fill complicated cavities. Depending on the amount used in the formulation, processing additives can replace completely the stearates. This will also result in the optimal performance in the compounds and final molded products. The surface is improved and the parts look more homogeneous and glossy.

Practical Hints and Suggestions
Recommended dosage levels: The proper use levels of processing additives, as with all additives, is of prime importance. Since the additive is designed to work with the whole compound, the required dose of the additive depends on the composition of the compound. But also the surface quality of the tool is important, in determining the correct dosage, so as to function properly as a mold release agent.

Point of addition: Processing additives should be incorporated first into the resin to achieve optimum performance. The formulation and the individual components can influence dispersion quality.

Combination with other additives: Until now, no negative influence with other additives has been observed.

Side-effects: The primary reason for using processing additives is the easier moldability of the compound and the improved homogeneity of the final molded part. It is important, to realize, that due to the building up of thixotropy, a compound is stabilized. This means also the resin-system itself (UP-resin and LS/LP-additive) are stabilized and separation is reduced. In some cases, a small effect can be found on the thickening. An approximate increase of 10% of the MgO content is usually sufficient to correct this effect.

Structure of Processing Additive

Mechanism: Compounding

Mechanism: Molding
Anti-Separation Additives

For improving the surface quality and dimensional stability of a molded part, shrink control additives are used. Low shrink additives like polystyrene or polymethyl-metacrylate are not stable after mixing with the UP-resin. Anti-separation additives improve the homogeneity of the resin system and keep the system in the filled status stable. In closed mold applications, often thermoplastic shrink control additives are used. PS and PMMA per example are not stable when mixed in the UP-resin. For the above reason, a new group of additives has been developed over the past few years – high molecular weight polymeric wetting and dispersing additives. Such additives differ themselves from the conventional low molecular weight polymers due to these considerably higher molecular weights which allow the attainment of a resin-like character. In addition, the newer additives contain a considerably higher number of adhesion groups. Because of these structural features, such additives can form durable adsorption layers upon many polymers. Stabilization arises from steric hindrance (as with the conventional products) in which solvated polymer chains are utilized. Optimal stabilization is possible only when such polymer chains are properly unfurled and therefore quite compatible with the surrounding resin.

**Working Mechanism**
This type of high molecular weight polymeric wetting and dispersing additive (figure 20) prevents separation of the LS-/LP-resin system and improves color homogeneity and color depth of the compound. Unsaturated polyester is reasonably polar (dipole moment 2.0–2.5), whereas polystyrene is relatively nonpolar (dipole moment app. 0.8). BYK anti-separation additives compatibilize this difference in dipole moment. Without using such a high molecular weight anti-separation additive, the well-dispersed thermoplastic particles will reagglomerate and separate again (figure 21). This group of BYK additives are block copolymers with UP-resin and LS-/LP-component compatible groups. That means, this class of additives will prevent phase separation by holding them in place and keeping them apart (figure 22).
**Practical hints and suggestions**

**Recommended dosage levels:** The proper dosage levels of anti-separation additives, as all additives, is of prime importance. Since the additive is designed to work with the resin system, the required dose of the additive depends on the composition of this system.

**Point of addition:** Anti-separation additives should be incorporated into the resin before other ingredients to achieve optimum performance. The formulation and the individual components can influence dispersion quality.

**Combination with other additives:** Until now, no negative influence with other additives has been detected. Mixing anti-separation with other ingredients before dosing to the resin system is not recommended.

**Side-effects:** The primary reason for using such a type of additive is the homogenization and stability of the compound. That results in an improved homogeneity of the molded part. But it is important, to realize, that due to better homogeneity of a compound, the shrinkage compensation will be more effective.

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**Final Remark**

All BYK additives described in this brochure were tested in different formulations. During the development of these additives we optimize them so that no negative side effects can be expected.

The table in figure 23 gives you some indication of which effects of the molded product are influenced by the BYK additives in the formulation.

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**Influence of BYK Additives on the Final Properties of Molded Parts**

<table>
<thead>
<tr>
<th>Wetting and Dispersing Additives</th>
<th>Processing Additives</th>
<th>Anti-Separation Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>Electrical properties</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>Mechanical properties</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>Surface</td>
<td>□</td>
<td>□</td>
</tr>
</tbody>
</table>

- □ strong
- □ no influence

figure 23
Products and Applications

BYK Additives
Additives are used during the production of coatings, printing inks and plastics to optimize the production process and to improve the quality of the final product.

Product Range Additives
• Additives to improve surface slip, leveling and substrate wetting
• Adhesion Promoters
• Defoamers and air release agents
• Foam stabilizers
• Processing additives
• Rheological additives
• UV-absorbers
• Viscosity depressants
• Waxes
• Wetting and dispersing additives for pigments and extenders

Application Areas
• Ambient curing resins (FRP)
• Architectural coatings
• Automotive OEM
• Automotive refinishes
• Can coatings
• Color coatings
• Color masterbatches
• Industrial coatings
• Leather coatings
• Marine paints
• Molding compounds
• Paper coatings
• Pigment concentrates
• Polyurethane foams
• Powder coatings
• Printing inks
• Protective coatings
• PVC plastisols
• Thermoplastics
• Wood and furniture coatings

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