

WETTING AND DISPERSING ADDITIVES FOR REACTIVE ADHESIVES AND SEALANTS

When increased filler content is required

Wetting and dispersing additives serve to either reduce viscosity or raise the filler content while keeping the viscosity constant. The use of functional fillers also opens up new formulation options, which in turn can lead to improved technical properties. Specially designed wetting and dispersing additives likewise help to prevent phenomena like phase separation and sedimentation.

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Reactive adhesives and reactive sealants cover a great variety of different chemical classes. The most important chemical classes of these systems are doubtlessly epoxides, polyurethanes, acrylates, silicones, and silane-terminated polymers. The application fields of these reactive adhesives and sealants are also very varied, cover-

ing transportation, building & construction industry, and electronics.

Besides all these different chemical classes and diverse applications, the reactive adhesives and sealants frequently have one thing in common: they almost invariably contain an inorganic filler. These inorganic materials may be classic fillers, such as calcium carbonate or silicon dioxide in the form of quartz powder or fumed silica. Besides

the above standard fillers, functional fillers, such as aluminum hydroxide as a flame retardant, metal powder for thermal conductivity, or carbon blacks, are additionally used. All these fillers must be dispersed as a first step. The second step is then to stabilize the particles sufficiently so that no re-agglomeration or sedimentation occurs.

Why wetting and dispersing additives?

With many formulas, the desire is to incorporate as large an amount of filler as possible into the system in order to optimize a specific technical property such as flame retardation or thermal conductivity still further. Unfortunately, large amounts of filler also create very high viscosities. With the required filler dosage, the viscosity of the system is so high that the latter cannot be processed any more.

The use of wetting and dispersing additives can help here. These additives help to achieve significantly lower viscosity (Figure 1). This effect on the viscosity enables technically improved formulas to be developed. Higher filler content is possible with the same viscosity, leading to better flame retardation or

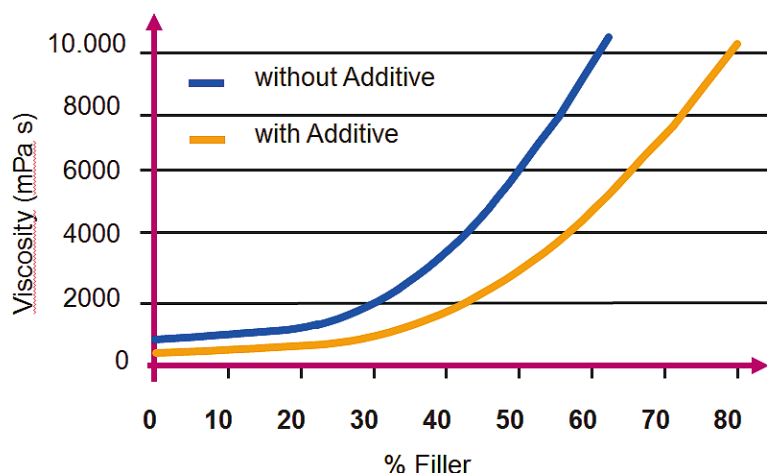


Figure 1: Increased viscosity with increasing filler content

better mechanical properties. If the development focus is on the price, then advantages are to be achieved here, too.

The phenomenon of phase separation or filler sedimentation occurs regularly with filled systems. This gives rise to problems with storage stability, or the customer is required to stir the container again prior to use. In this instance, too, the correct choice of wetting and dispersing additives produces a perfectly stabilized adhesive system without separation or sedimentation.

Mode of action

A distinction is drawn between different groups of wetting and dispersing additives, depending on the mode of action. The deflocculating wetting and dispersing additives achieve a clear reduction in viscosity. These additives usually possess a linear structure and have on one side of the molecule an anchoring group that attaches to the filler surface, while the other side of the additive is designed to be compatible with the binder. For the majority of inorganic fillers in the adhesives and sealants field, acidic anchoring groups are highly suitable. Carboxylic acid or phosphoric acid groups are excellent for basic fillers such as calcium carbonate or aluminum hydroxide. With the binder-compatible part of the additive, there is a large variety of alkyl chains, polyurethanes, polyethers or polyesters to choose from.

The anchoring group of the additive attaches to the surface of the filler particles and the binder-compatible remainder aligns itself with the binder. Consequently, the filler particles are kept at a distance due to steric forces. The particles can no longer come as close and interact with each other (Figure 2). The viscosity of the system is reduced significantly.

With the controlled flocculating wetting and dispersing additives, the structure of the additives looks very different.

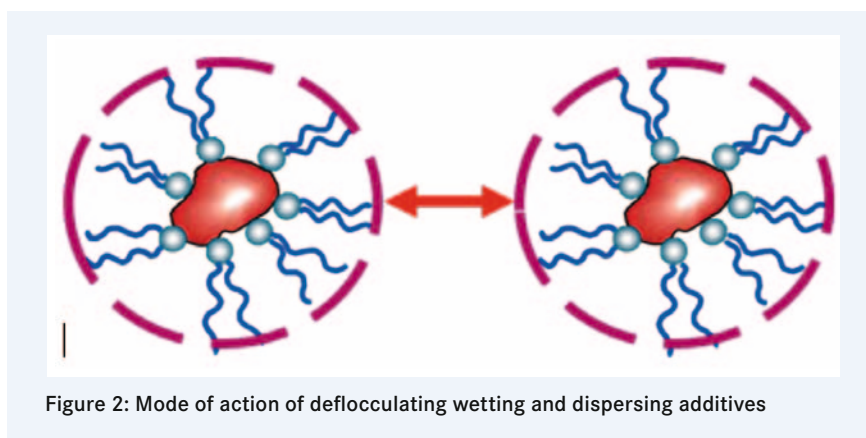


Figure 2: Mode of action of deflocculating wetting and dispersing additives

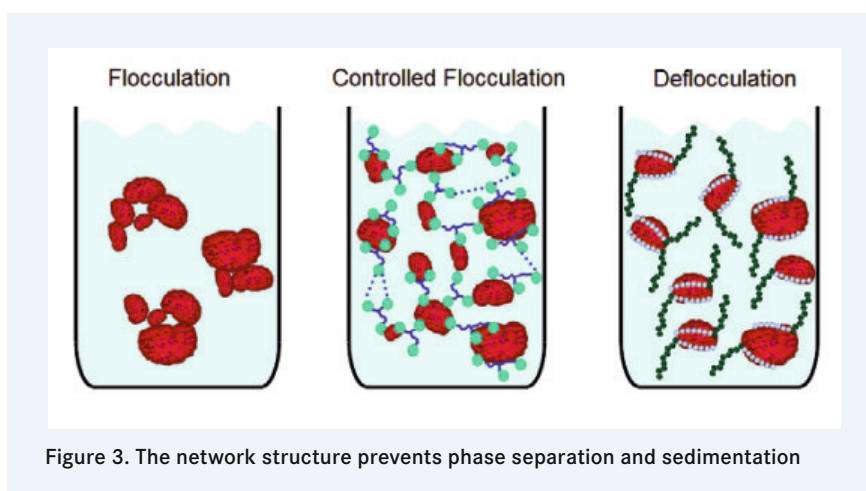


Figure 3: The network structure prevents phase separation and sedimentation

PUR formulation	Control	With additive
Castor oil	32,5	32,5
Defoamer	0,3	0,3
Wetting & dispersing additive	-	0,65
5 μm CaCO_3	65	65
Zeolith	2,5	2,5
Wetting & dispersing additive based upon filler	-	1 %

Table 1: Polyurethane adhesive formulation

The additives do not only have a filler affinic group but are also multifunctional. This enables the additives to develop an interacting network structure and to stabilize the particles through this

Reduction in viscosity

Several examples are listed below which show the extent to which the viscosity of a filled adhesive or sealant can be re-

duced by the use of wetting and dispersing additives.

The first example is a two-component polyurethane adhesive. The polyol component is based on a castor oil, which is filled with 65% of a 5 μm calcium carbonate. The formula details are listed in Table 1. With the “Control” viscosity curve in Figure 4, no wetting and dispersing additive has been used what-

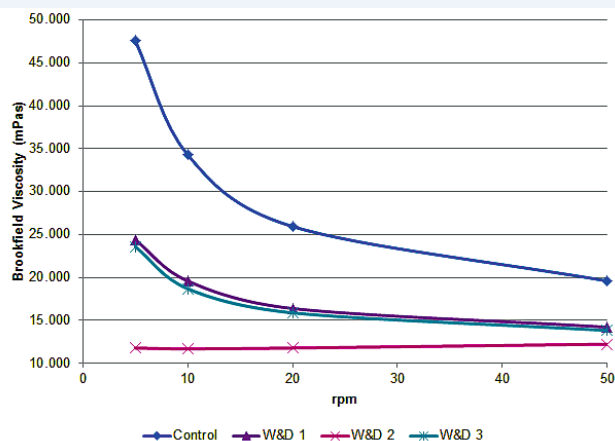


Figure 4: Reduced viscosity from deflocculating wetting and dispersing additives

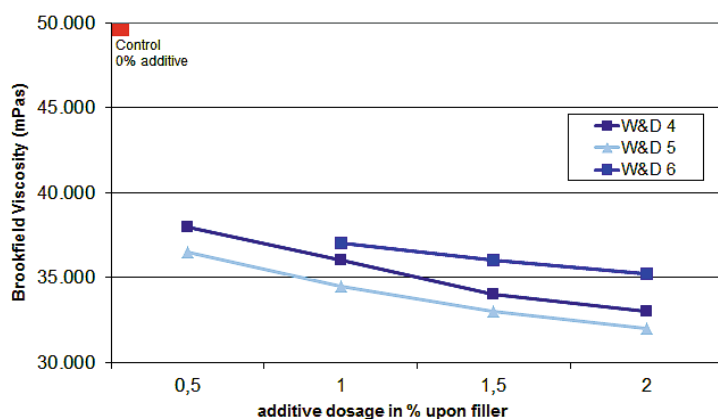


Figure 5: Reduced viscosity as a function of the additive dosage

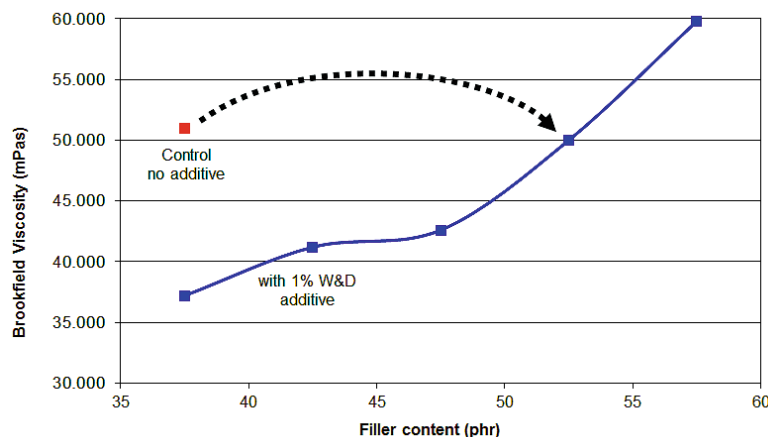


Figure 6: Increase of the filler concentration

soever. The curve exhibits a shear-thinning behavior. The viscosity curves with wetting and dispersing additives are at significantly lower viscosities. The viscosity at 20 rpm on the Brookfield viscometer is halved in this instance! It can also be seen from the progression of the viscosity curves that certain additives lower the viscosity level while having no effect on the fundamental viscosity profile. The shear-thinning behavior is preserved. Other wetting and dispersing additives are more likely to produce Newtonian flow behavior and thus, especially in the low shear range, a very different effect than would happen without any additive. Advantages may result during pumping and in the leveling after application. However, it should be noted, particularly with low absolute viscosities, that there is no problem with sedimentation.

Owing to the use of wetting and dispersing additives, a 40% viscosity reduction is no rare occurrence, regardless of the type of filler. With low filler content, increased viscosity due to the introduced filler is negligible and therefore cannot be dramatically affected by the additives. The higher the filler content, however, the greater is the reduced effect of the additive.

The dosage of 0.5 to 1% wetting and dispersing additive based upon the filler quantity is a rule of thumb for the majority of fillers with a $> 2 \mu\text{m}$ particle size. With finer particles that have a bigger specific surface, a higher dosage of the additive is necessary to cover the surface adequately. The additive should always be distributed homogeneously in the system before the filler is added.

The second example shows a heat-cured bisphenol A epoxy adhesive. To make the system fully flame-retardant, a very fine-particle aluminum trihydroxide (ATH) has been used. The filler content is 37.5 phr.

It is clear from Figure 5 that the viscosity has been reduced by approx. 35%.

Polysulfide formulation	Control	With additive
Thiokol polymer	100	100
Benzoate plasticizer	80	80
Wetting & dispersing additive	-	2
2 μm CaCO_3	200	200
Wetting & dispersing additive based upon filler	-	1 %

Table 2: Polysulfide formulation

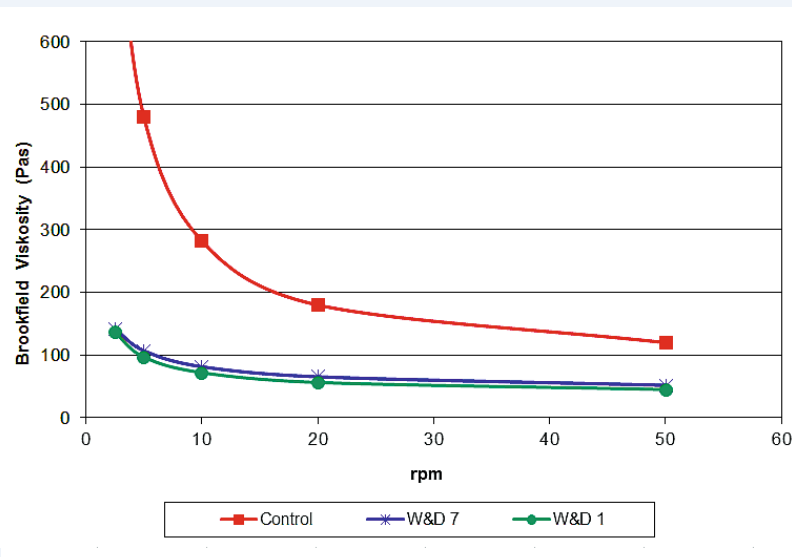


Figure 7: Reduced viscosity in a polysulfide system

As a very fine-particle ATH is involved, greatly reduced viscosity is associated with a higher additive dosage. Above a 2% additive dosage, however, no further significant viscosity reduction is to be expected.

Higher filler dosage with the same viscosity

As referred to above, there is frequent interest in incorporating greater filler content into the system in order to make specific improvements to technical properties. Figure 6 is concerned with the question “How much more filler can be added while keeping the viscosity the same?” The starting point here was a heat-cured epoxy adhesive, which was filled with 37.5 phr ATH and contained no wetting and dispersing ad-

ditive at all. 1% additive based upon filler was used, and then the filler content was gradually increased with the aim of achieving the initial viscosity without an additive.

The results show that approx. 40% more ATH filler can be added and the viscosity stay the same. This advantage may be transferred to other systems and other fillers to optimize their technical properties further, such as thermally conductive adhesives that are filled with metal powders.

Reduced viscosity with sealants

In the area of sealants, Figure 7 shows a polysulfide system. Polysulfide is primarily used as a sealant in insulating glass panels or as a self-leveling sealant in the construction industry. The base



Figure 8: Filler stabilization by controlled flocculation

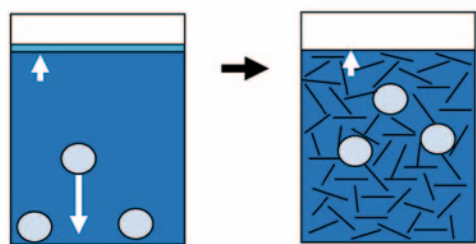


Figure 9: Mode of action of layered silicates for filler stabilization

polymer consists of a Thiokol polymer, benzoate plasticizer and approx. 50% of a 2 µm calcium carbonate filler.

The viscosities of the samples containing wetting and dispersing additives are also significantly lower here than they are without. This reduction in viscosity is interesting for filled, self-levelling polysulfide sealants in particular, offering more flexibility in the formulation.

What about phase separation or sedimentation?

Besides reducing viscosity, another application of wetting and dispersing additives is the avoidance of phase separation or the prevention of sedimentation. Controlled flocculating wetting and dispersing additives are used here. Because of their multifunctional anchoring groups, they attach to the filler on the one hand and form a three-dimensional network on the other. This network

stabilizes the filler particles, preventing separation and sedimentation.

The following photographs in Figure 8 depict the polyol side of a 2-component PUR adhesive. The high specific density of the current fillers makes them prone to sedimentation during storage.

Especially in large containers, such as drums or IBCs, phase separation on the surface is undesirable. Sedimentation from filler sediments is very hard to stir up again. Frequently, the end customer has no suitable equipment to stir the system again homogeneously.

Alternative to stabilization in powder form

Besides the liquid wetting and dispersing additives, powdery layered silicates are also suited to filler stabilization. Owing to different charges on the edges and on the platelets of the layered silicate, a house of cards structure is formed. This house of cards stabilizes the system and

prevents the sedimentation of filler particles (see Figure 9).

The layered silicates increase the viscosity at very low shear rates. The structure will collapse with low shearing, with the result that very low application viscosity is achieved. The liquid wetting and dispersing additives always need to be matched to the existing filler particles and the binder system. The layered silicates offer a somewhat more universal approach, as only the dosage has to be adjusted to keep the filler particles in suspension.

Summary

Wetting and dispersing additives enable a new direction to be taken in terms of the formulation of reactive adhesives and sealants. The limiting of the filler content, due to the increase in viscosity, can be significantly postponed and made more flexible. As a result, new formulations are possible, especially with functional fillers such as ATH for flame-retardant properties or metal powders for thermal conductivity. The deflocculating wetting and dispersing additives enable a lower viscosity to be achieved in filled systems, which gives the formulator much more freedom. The controlled flocculating wetting and dispersing additives, by contrast, are used to prevent separation and sedimentation. Alternatively, layered silicates may also be used here for stabilization, which develop a specific rheological profile that nevertheless exhibits a very low viscosity level during application. ■

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