

# Defoamer Technologies

## AGITAN<sup>®</sup>

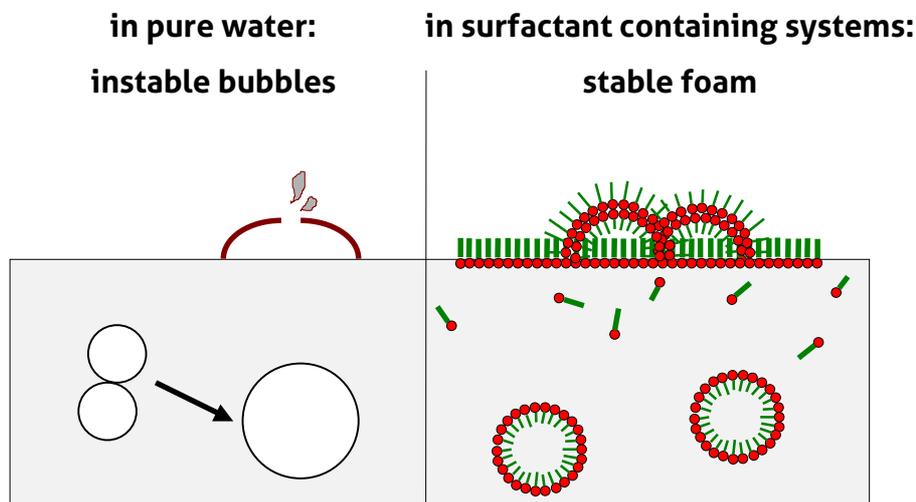
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## 1 Introduction

The introduction and stabilisation of hydrophobic materials like binder molecules, pigments and fillers into waterbased coating systems has to occur through surface active materials. Binder molecules of aqueous dispersions are stabilised by emulsifiers; pigments and fillers are incorporated by wetting and dispersing agents into an aqueous medium. All surface active materials, however, tend to foam in aqueous systems.

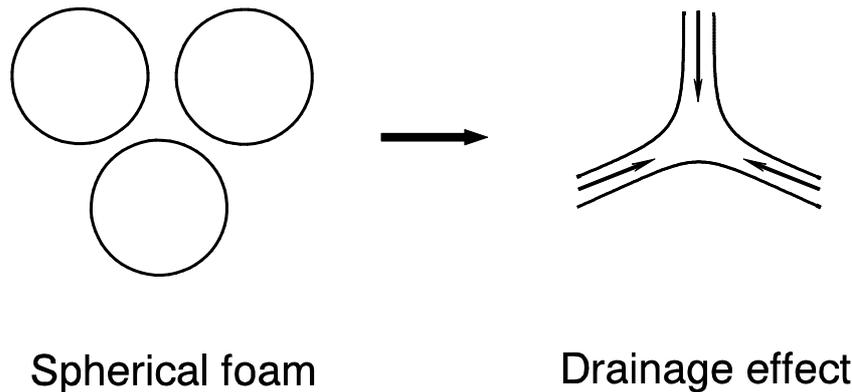
The stabilisation of bubbles by surfactant molecules is the main assumption for foam formation. The extend of the creation of foam is influenced by other factors: formulation ingredients, production and application methods and also the substrate can support the creation of foam and increase or decrease the efficiency of a defoamer.

In a pure liquid (water) where no surfactants are present, air bubbles rise to the surface and burst. The interfacial tension between the air and the liquid is too high and the bubble cannot be stabilised. However, in systems where surface active substances are present, air bubbles are stabilised like hydrophobic particles by surfactant molecules (figure 1). These surfactant molecules, having a hydrophilic-hydrophobic character, form a layer around the bubble, orientating the hydrophobic end towards the air (bubble) and the hydrophilic end towards the water. Thus, the interfacial tension between bubble and liquid is lowered and stabilised. The bubble rises to the surface, where also a layer of surfactant molecules is present between the air and the liquid interface. A stable double layer is formed including the surfactant layers of the bubble and the surface. This layer consists of the monolayer of surfactant molecules at the air-liquid interface of the bubble and the monolayer of surfactant molecules which cover the liquid-air interface.<sup>[1-5]</sup>



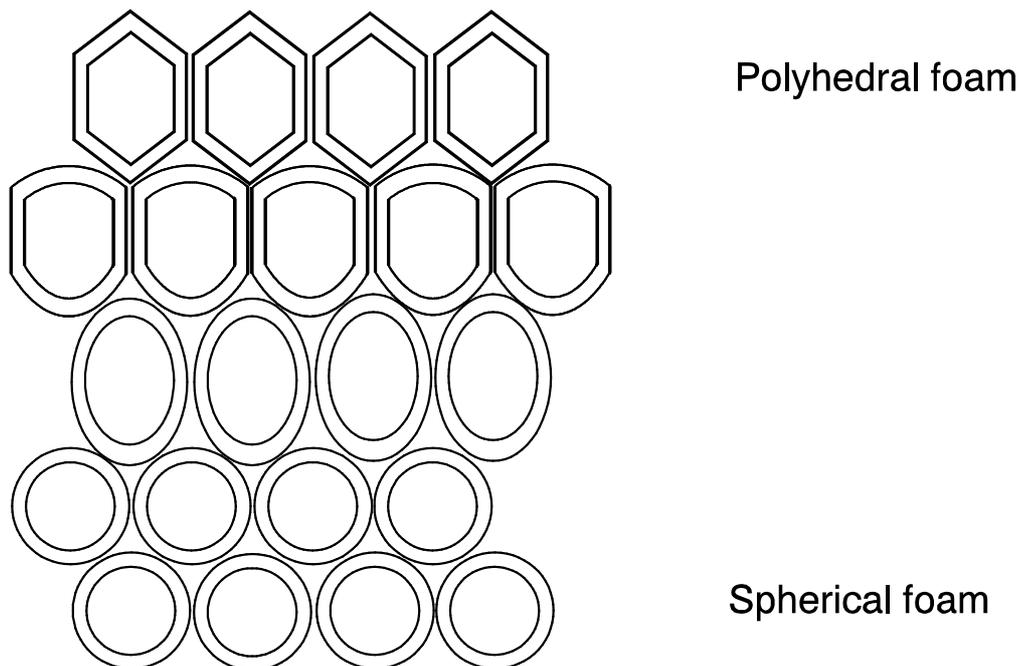
**Figure 1:** Stabilisation of bubbles in surfactant containing water

According to the mechanism of foam formation the individual bubbles form a close spherical packing. Due to osmotic processes between the bubbles a drainage effect causes the removal of water from the interface between the bubbles (figure 2). This water is collected in the void space between the bubbles. Due to this effect, a distortion of the spherical layer towards an octahedral geometry can occur by forming narrower distances between the double layers (figure 3). This so called polyhedral foam consists of hexagonal close packed air.<sup>[6, 7]</sup>



**Figure 2:** Narrowing of bubbles due to the drainage effect

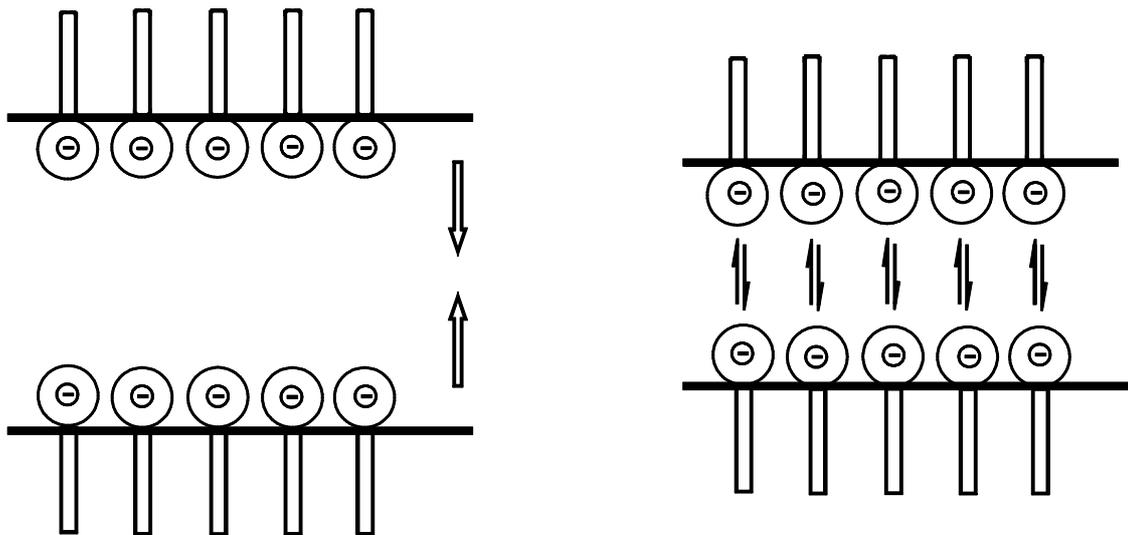
Two other effects allow to stabilise the foam. The Marangoni effect describes the tendency to generate the energetically most favourable condition. In the case of a lack of surfactant molecules in one part of the liquid surface or the bubble the surface tension is altered in this region and therefore different to other parts. The effort of the system is to restore the former surface tension by migration of surfactant molecules to this part (self curing effect).



**Figure 3:** Distortion of the spherical layer towards an octahedral geometry

The second effect is an electrostatic repulsion of equally charged surfactant molecules from two different monolayers. Due to the narrowing of the two layers in the lamellae by drainage effects a collapse of the two layers and therefore a burst of the bubble would result. This narrowing is prevented by electrostatic forces of charged parts of the surfactant molecules which keep the monolayers in an equilibrium distance (figure 4).

In practice the described stabilisation of foam to a stable polyhedral foam does only occur in minor occasions in paints and similar coatings during production and application. Normally, problems arise during production and application due to individual bubbles which lead to surface defects in the applied film.



**Figure 4:** Narrowing of the monolayers and (electrostatic) repulsion

Modern defoamer technology helps to overcome foam problems because the mechanism of foam formation and destruction is understood. The number of possible ingredients and therefore the high number of their combinations of a coatings formulation (e.g. binder, emulsifiers, wetting and dispersing agents, solvents, thickeners) have prevented until now a method to predict exactly a certain type of defoamer for a given formulation or problem. Additionally, influences from the system on the defoamer increase the uncertainty for a defoamer prediction. Empirical work, however, has led to great experience in the application of defoamers and helps to find the right defoamer for a given foam problem.

## 2 Basics: Foam formation

### 2.1 Formation of foam during production

During the stirring and dispersing process air is introduced into the coating systems. Vigorous stirring during the grinding of formulation ingredients leads to the incorporation of air and its stabilisation due to surfactants. Air is liberated at the same time in the grinding process due to the wetting of the pigment and filler surface and the simultaneous exchange of air by water due to wetting agents. At this stage of production it is important to use an efficient defoamer which unifies the small, single bubbles to bigger ones supports the transport of air bubbles outside the system.

The requirements for a defoamer during production depend on the characteristics of the coating system and the type of production. During the grinding process, where high shear forces are applied, vigorous stirring is required and a large amount of air is incorporated. A high efficient defoamer which resists the shear forces and therefore is difficult to emulsify has to be used. These defoamers are relatively difficult to incorporate because low or no quantities of emulsifier are used to support the incorporation in the medium. Therefore the active particle size of the defoamer can be kept which is not the case with defoamers which are easy to incorporate. Their active particle size is lowered due to applied shear forces (see also figure 7).

In low viscous and/or low pigmented systems defoamers which are hard to emulsify generally cannot be used as they might cause problems in the surface of the applied film or they might tend to separate. Here, defoamers which are easy to emulsify have to be used.

This presentation however, is only a rough classification because limits are fluent and depend of the special system.

An efficient defoamer is important from an economical point of view: production times are longer if foam is formed during fabrication. A large amount of trapped air in the grinding process will reduce the efficiency of the transfer of shear forces: air acts like an airbag between the stirrer (mixing arm) and the pigment agglomerates. Times to obtain the same grinding quality are longer in the presence of foam. Filling quantities are not reproducible if changing quantities of air are present.

In the letdown phase where temperature and shear sensitive binders are added the stirring is less vigorous. Here, the addition of defoamers removes air from the system and prevents the stabilisation of foam bubbles. The emulsifiers which are incorporated together with the binder tend to stabilise foam.

## **2.2 Formation of foam during pumping and filling**

During processing (pumping, filling, transport) air can also be introduced into the system due to the movement at the air/liquid interface. The coating is also pumped, transported and moved in different application methods like printing, curtain coating or dipping. Not only the foam which is formed during production but also later on, while pumping and filling, has to be destroyed. The defoamer which was acting already during production therefore has to give sufficient efficiency to destroy foam or prevent its formation.

In order to meet quality control requirements a constant density of the coating is necessary for a constant filling of the cans. Furthermore, the optical aspect of the paint is important as customers do not appreciate paint cans with foam on the surface. During storage the defoamer therefore has to be still active.

## **2.3 Formation of foam during application**

The methods of application and the kind of substrate have a strong influence on the tendency of foam formation during application. Especially porous substrates like walls, wall paper, untreated wood etc., show an increasing tendency to form foam. The application tool (brush, roller, spray gun etc.) has an influence just as important as the substrate and may generate or even prevent the formation of foam.

Spray application leads to high requirements for the performance of a defoamer since the coating is saturated with air after leaving the nozzle. The defoamer must be efficient in immediately destroying microfoam formed on the substrate.

# **3 Defoamer characteristics**

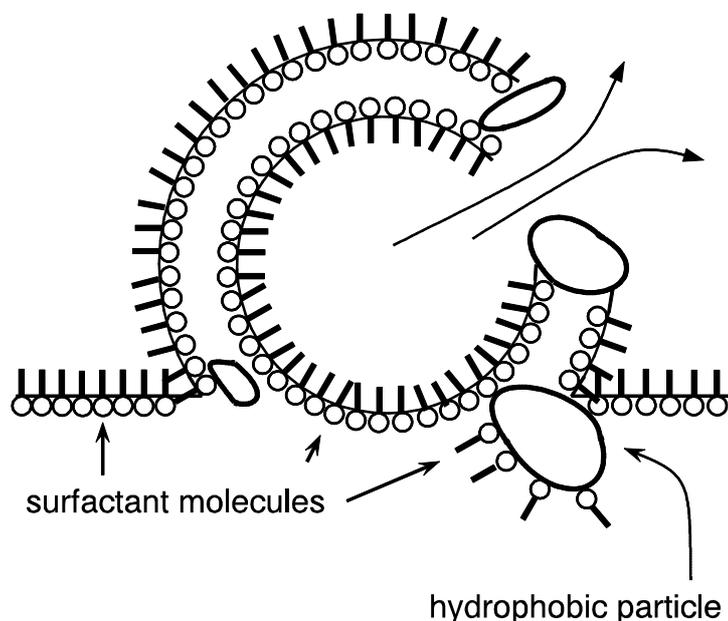
## **3.1 Defoamer composition**

In general, defoamers consist of several compounds, which in total are not compatible with the coatings medium. Problems arise with defoamers that are too compatible with the system, which means that they are inefficient. Otherwise, if they are too incompatible in the system, these defoamers might be highly efficient but they will cause problems in the applied film. The ideal solution in the application of defoamers is to find the best balance between compatibility and incompatibility of the defoamer for a maximum of efficiency.

Defoamers are multi-component systems with different groups of functional ingredients. There are three principal classes of components: carriers, with a share of 75 - 90 %, hydrophobic ingredients, with a content of 5 - 10 % and other special substances (e.g. biocides, thickeners, emulsifiers) with 0 - 20 % in the formulation.

**Carriers** generally are different kinds of oils: most versatile and least costly are mineral oils. Beside these, paraffinic (medical white) oils are used in order to meet health regulations (BGVV/FDA) and for food and potable water applications. Furthermore, vegetable oils (biologically degradable and for low VOC or 0 VOC paints), silicone oils, polysiloxanes and water are used as carriers. Fatty acids, fatty alcohols and polyvinyl ethers are also used.

The purpose of the carrier is to spread on the surface in order to remove the layer of surfactant molecules. Therefore, it has a lower surface tension than water. The other important purpose is to carry the hydrophobic ingredients of the defoamer formulation to the double layer. Therefore, carriers have to be insoluble and incompatible with the solvent (water) in order to rise to the surface. This monolayer formed by the defoamer ingredients must have a reduced surface elasticity compared to the original surface elasticity of the foam bubble double layer.



**Figure 5:** Destruction of the double layer by hydrophobic particles

**Hydrophobic ingredients** can be used in a liquid or solid form. In a liquid form they exist as emulsion droplets. Particles are always hydrophobic materials with a particle size between 0.1 and 20  $\mu\text{m}$ . The particle size is an important factor in order to enter the double layer. If the particle size is too small, the effectiveness of the particle is reduced significantly because water can enter into the double layer and dilute the concentration of the defoamer particles. If the particle size is too big, the particle can not enter into the double layer and a collapse of microbubbles into macrobubbles can not occur (see also figure 7).<sup>[8-10]</sup>

The most important task of hydrophobic ingredients is to absorb surfactant molecules from the double layer by which the surface tension is increased and the bubble bursts.

The concentration of the particles in a defoamer formulation is limited due to the fact that the total concentration of surfactant molecules has to be kept over a limit in order not to destabilise the whole emulsion, which would lead to a flocculation of the polymers.

Compounds used as hydrophobic particles are waxes, hydrophobic silica, metal soaps and also polypropylene glycols, amides and polyurethanes.

**Emulsifiers** are of great importance because they regulate the compatibility of the defoamer in a coating system. Depending on the emulsifier the defoamer is dispersed to a certain extent and develops its efficiency depending on the particle size. Therefore, the emulsifier is the most important ingredient in finding a balance between compatibility (= inefficiency) and efficiency (= incompatibility) of the defoamer in a coating system. Furthermore, as emulsifiers are also surface active materials it is desired that they have a low tendency to foam.

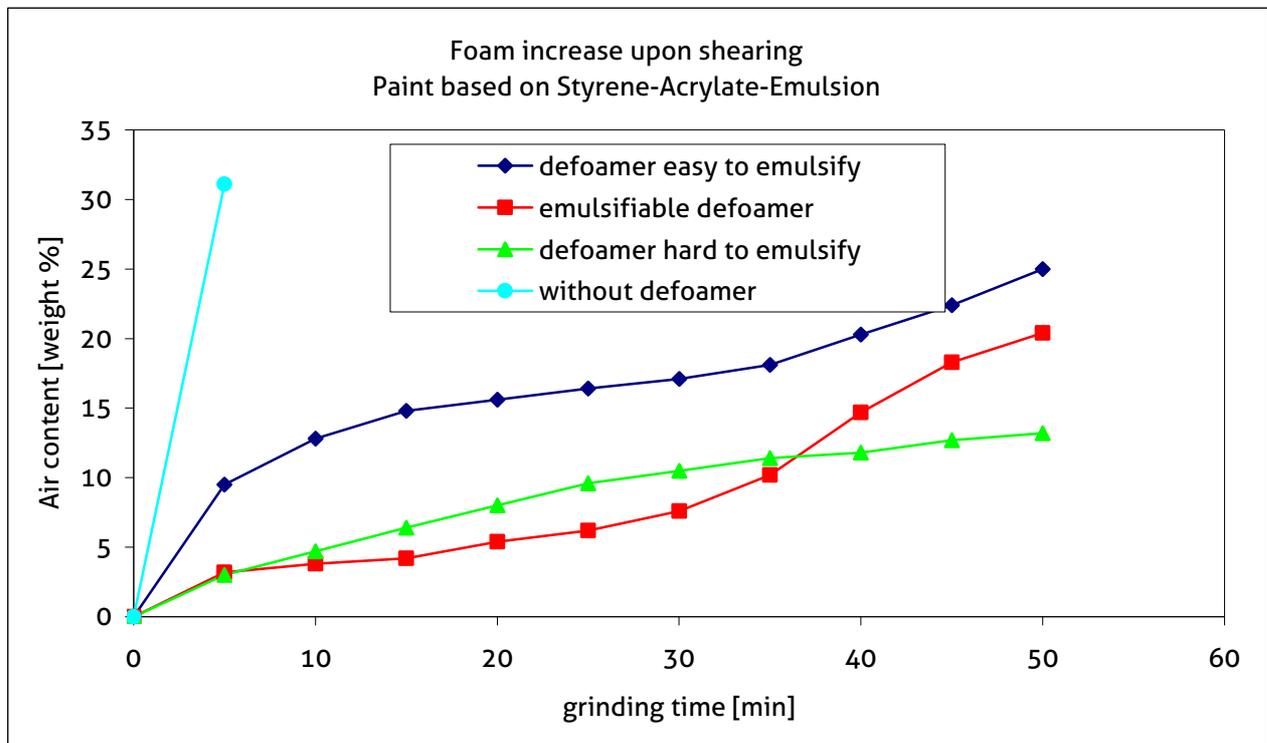
**Other materials** present in a defoamer can be biocides, thickeners or protective colloids.

### 3.2 Influence of mechanical forces on different defoamer types

The efficiency of defoamers in the system to defoam depends from the balance between compatibility and incompatibility. Not only the defoamer but also the system in which the defoamer is used influence this balance. If water is used as reference, defoamers can be classified in three groups: easy, fair and hard to emulsify.

Defoamers which are easy to emulsify are such types, which can be homogenised in water only by shaking and which keep stable over a longer period without separating. Defoamers which are difficult to emulsify recover immediately after shaking a two-phase system. Other defoamers range in between these limits. Depending on pigmentation, viscosity and other parameters of the system which has to be defoamed defoamers for definite applications can be recommended.

The best efficiency is obtained when the defoamer just can be incorporated (emulsified) but compatible enough in order not to produce any surface defects. As the ease of incorporation depends on the system to be defoamed the right defoamer has to be found, in case of uncertainty, by trials.



**Figure 6:** Behaviour of different defoamer types under shear forces

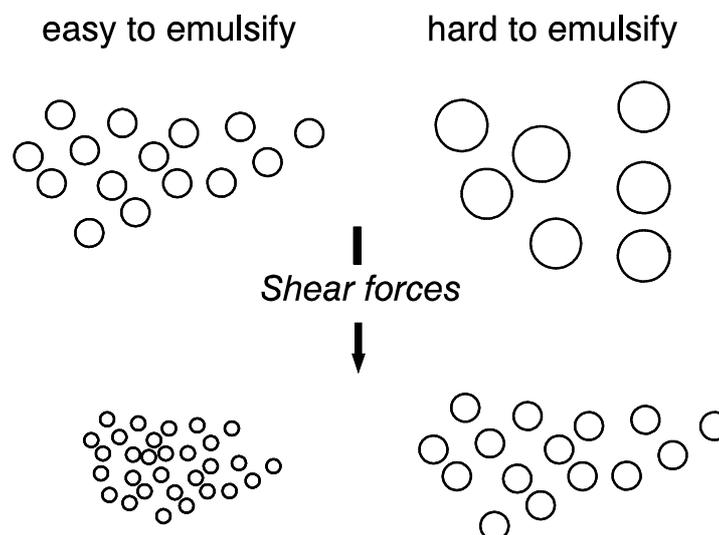
Figure 6 shows a paint of high pigmentation based on styrene/acrylic binder in which three types of defoamers are exposed a shear stress of 50 minutes and the air content of the samples is measured in 5 minute intervals. As the figure shows the sample without defoamer shows already after 5 minutes a strong increase in air. In contrast, the defoamer which is easy to incorporate shows a strong reduction of the incorporated air, which is stabilised on a certain level before losing efficiency after approx. 35 minutes.

The defoamer of medium emulsifiability shows especially at the beginning a high efficiency because it is easy to incorporate but more resistant to shear forces than the easily emulsifiable defoamer. After a certain period of having applied shear forces, however, this defoamer also loses efficiency.

The defoamer which is difficult to incorporate is more efficient than the easy emulsifiable defoamer but less efficient at the beginning than the defoamer of medium emulsifiability. In contrast to the two other types the defoamer of difficult incorporation does not lose efficiency after a longer period under shear forces. This is important when after the mechanical treatment during production the efficiency of the defoamer during pumping, filling, storing and especially under application is required. The type of defoamer which is difficult to incorporate in this case shows the advantages to suppress the formation of foam or to destroy the bubbles which are created during these processes rapidly and without leaving defects.

### 3.3 Particle size of defoamers

The particle size of defoamers is important for the efficiency in the system to be defoamed. Particles are all hydrophobic compounds of the defoamer which enter into the lamellae as solid particles or liquid droplets and which absorb surfactant molecules from the interface. Due to this change in the interfacial tension they cause the burst of the bubbles.



**Figure 7:** Particle size of defoamer droplets under shear forces

A defoamer which contains higher quantities of emulsifiers and which is easy to incorporate and to stabilise in water, behaves under shear forces in that way that even smaller particles are obtained. The efficiency however is lost because these droplets become inefficient in the foam lamellae.

On the other hand the particle size of defoamers which are difficult to incorporate and which contain no or small quantities of emulsifiers, is rather too big to enter the lamellae. This defoamer type needs the shear forces in order to obtain an efficient particle size. As a result, these defoamer types may appear less efficient at the beginning under shear forces compared to defoamer with higher contents of emulsifiers (figure 6). At the end a better efficiency is obtained during storing and application.

## 4 Experimental test methods

- **Red Devil Test**

The "Red Devil Test" is the standard test method in MÜNZING CHEMIE to measure the air incorporated in coatings of both, low and high viscosity systems. Samples are shaken with different types of defoamers in a red devil mixer which allows intensive shaking in a reproducible way during which air is incorporated into the sample. Defoamer concentrations and periods of shaking can be adapted to necessary requirements. The density of the sample, as a function of incorporated air, is determined after shaking and compared with the value of an untreated sample without incorporated air. The values are given as percentage of incorporated air.

The air content is calculated in the following way:

$$\text{Air content [\%]} = 100 - \left( \frac{b}{a} \cdot 100 \right)$$

with b = weight of the treated sampled

and a = weight of the untreated sample (50 ml pycnometer volume each).

The test can be repeated with already shaken samples that have been stored in order to determine long term stability of the defoamers.

- **Dissolver**

For all kinds of coatings, but especially for systems of lower viscosity, the dissolver test is used. Apart from the efficiency of the defoamer its tendency to separate can be determined in this test method. A 50 ml sample is filled into graduated glass cylinders of 250 ml. The sample is stirred with a toothed dissolver disc for a certain period of time. This period is adapted to the requirements which are given by the sample. The foam formation is measured just after stirring and the resistant foam is determined after a certain period of time. The first value then indicates the efficiency of a defoamer to prevent the formation of foam whereas the second value indicates the efficiency to destroy the foam already formed. After storing of these samples for a certain period it is possible to judge the tendency of the defoamer to separate.

- **Levelling on glass plates/compatibility**

Coating samples obtained from the red devil or dissolver test are applied 24 hours after shaking or stirring with defined film thickness on a degreased glass plate with a blade (25 - 100 µm). Evaluation of the surface aspect is carried out under wet and dry conditions in order to judge the compatibility between the defoamer and the coating system. Defects like pinholes, orange peel, craters, fisheyes etc. indicate insufficient compatibility of the defoamer in the given system and the glass substrate. This can be caused by general incompatibility, overdosage, bad substrate wetting and other effects and does not have to occur in the application for which the coating normally is used (e.g. walls, wall paper substrates, etc).

- **Roller and brush application**

A defined amount of paint is applied on PVC foil, PE foil, wood, paper etc. depending on the purpose of the coating. The application tool is a highly structured foam roller or a brush. Especially with the roller it is possible to incorporate large quantities of air. The creation of foam during application is judged as well as the efficiency of destruction while and after drying. The conditions of the coating in wet and dry state after roller application gives indications of the defoamer activity.

- **Spray application**

The spray application is carried out for industrial lacquers and all other spray applied coatings in order to evaluate the efficiency of the defoamer under spray conditions, especially regarding microfoam formation. During the application there is a high saturation of air in the coating. The resulting surface properties are evaluated and lead to indications of the defoamer efficiency.

- **Gloss**

Certain defoamer components can exhibit gloss reducing properties. Especially hydrophobic silica and waxes in high concentrations may reduce gloss in gloss paints and lacquers. Gloss values are measured in gloss paints to avoid the recommendation of a defoamer which reduces gloss.

## 5 Examples

Apart from different formulation types and their peculiarities in application other influences can determine the efficiency of a defoamer. In this chapter the effects of isolated properties like binder type, emulsifier system or dispersing agent on the defoamer performance are studied<sup>[13]</sup>.

### 5.1 Influence of different binder types

The binder type can have a strong influence on the performance of a defoamer. If only the efficiency of a defoamer in a dispersion is tested and further effects like separation or stability are ignored, strong differences in the performance of defoamers of different chemical composition will be obtained.

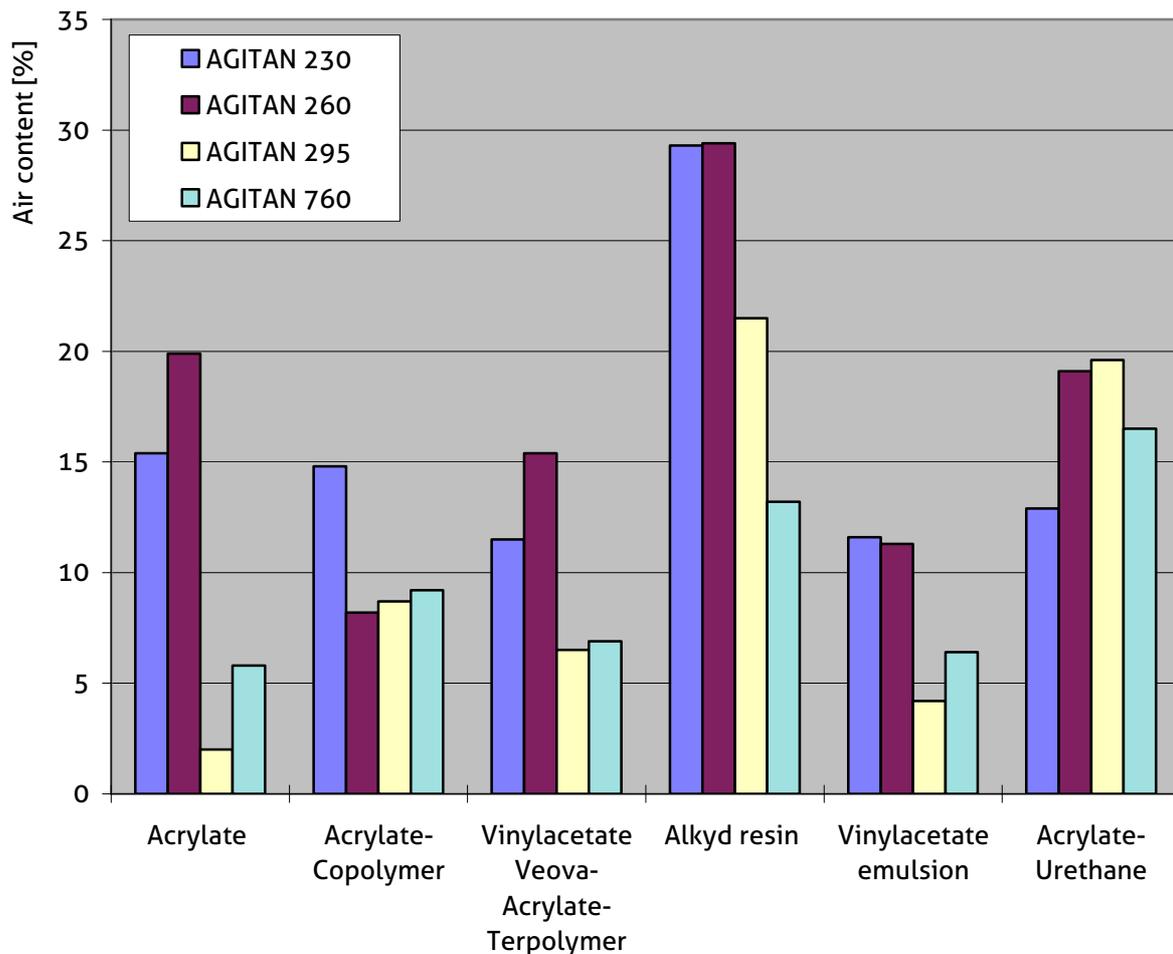
Table 1 shows the results of experiments, in which several different defoamers are tested in different binder types. The given values are air content in %.

	Acrylate	Acrylate-Copolymer	Vinylacetate Veova-Acrylate-Terpolymer	Alkyd resin	Vinylacetate emulsion	Acrylate-Urethane
<b>AGITAN® 230</b>	15.4	14.8	11.5	29.3	11.6	12.9
<b>AGITAN® 260</b>	19.9	8.2	15.4	29.4	11.3	19.1
<b>AGITAN® 295</b>	2.0	8.7	6.5	21.5	4.2	19.6
<b>AGITAN® 760</b>	5.8	9.2	6.9	13.2	6.4	16.5

**Table 1:** Influence of the binder type on the defoamer efficiency (values as air content in [%])

As can be seen from table 1 and figure 8 the performance of the defoamers in different binder types can vary widely. In the pure acrylate the efficiency of the best defoamer is 10 times better than from the less efficient. In the acrylate-urethane binder differences in the performance of these two defoamers are smaller and in this case both are less efficient than the most efficient defoamer.

As can be seen from this investigation no general prediction can be made indicating the best defoamer type for a certain binder type.



**Figure 8:** Influence of the binder type on the defoamer efficiency

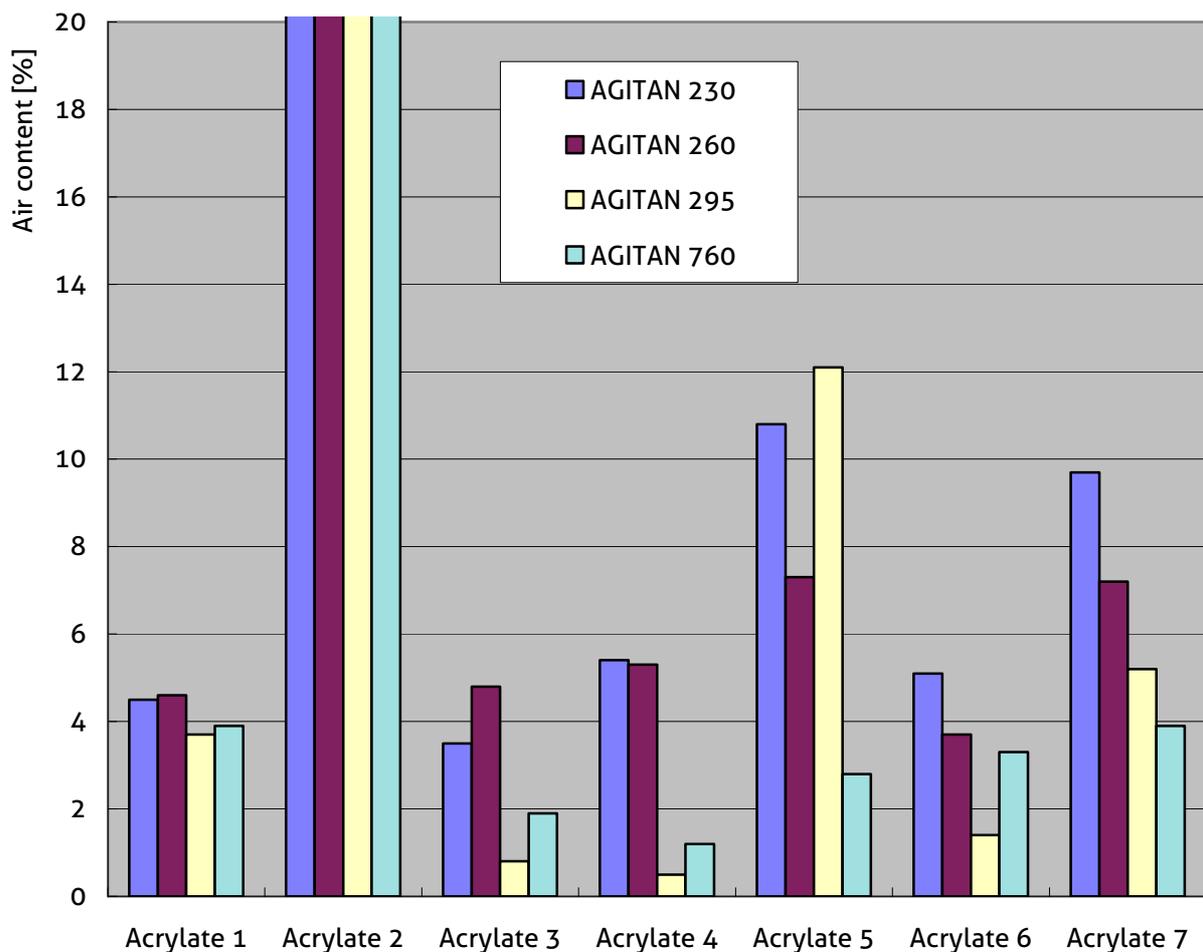
## 5.2 Influence of different emulsifier systems

The influence of the kind of binder on the performance of a defoamer is already strong. But also within the same binder type the performance of defoamers can vary strongly, due to the fact that different emulsifier systems are used.

As example several pure acrylic binders are investigated in table 2 regarding the defoamer efficiency. The type of emulsifier and the content of emulsifier in the binder has a tremendous influence on the defoamer performance (figure 9).

	Acrylate 1	Acrylate 2	Acrylate 3	Acrylate 4	Acrylate 5	Acrylate 6	Acrylate 7
<b>AGITAN® 230</b>	4.5	45.47	3.5	5.4	10.8	5.1	9.7
<b>AGITAN® 260</b>	4.6	39.0	4.8	5.3	7.3	3.7	7.2
<b>AGITAN® 295</b>	3.7	51.3	0.8	0.5	12.1	1.4	5.2
<b>AGITAN® 760</b>	3.9	47.4	1.9	1.2	2.8	3.3	3.9

**Table 2:** Influence of the emulsifier type on the defoamer efficiency (values as air content in [%])



**Figure 9:** Influence of the emulsifier type on the defoamer efficiency

Figure 9 demonstrates that there is a strong difference in the type and quantity of emulsifier as in acrylate 2 very high values of air content are measured in comparison to the other acrylates.

In acrylate 1 all defoamers show similar performance whereas in the other acrylates the efficiency of the defoamers vary stronger.

The performance of a certain defoamer can change with every binder: in acrylates 3, 4 and 6 the AGITAN<sup>®</sup> 295 shows the best result with very low air content levels compared to the other defoamers tested. In contrast, in acrylate 5 it is the less efficient one. This reveals the fact that no general predictions can be made.

### 5.3 Influence of the formulation

A strong difference in the performance of defoamers can be observed if the defoamer efficiency is determined in a pure emulsion or in a formulated paint containing this binder. Table 3 shows the results of the defoamer tests of this comparison.

In the case of the pure emulsion AGITAN<sup>®</sup> 760 shows the best efficiency of the defoamers displayed in the table. There is a big difference to the defoamer with lowest efficiency.

If a lacquer is produced out of this emulsion and the same defoamers used in a test to determine their efficiency completely different results are obtained. The best result is obtained with AGITAN<sup>®</sup> 260 which shows medium efficiency in the pure emulsion. The defoamer of lowest efficiency in the lacquer is AGITAN 700, which had regular results in the pure emulsion. In the formulated lacquer the differences in defoamer efficiency are closer than in the pure emulsion.

Formulation components and properties like wetting and dispersing agents, pigmentation, type of thickener, etc. have a strong influence on the performance of a defoamer and no general derivation can be made, as demonstrated in table 3. Only an experimental test can give the required information.

defoamer	dispersion air content [%]	lacquer air content [%]
AGITAN <sup>®</sup> 230	11.3	2.6
AGITAN <sup>®</sup> E 256	5.1	5.1
AGITAN <sup>®</sup> 260	9.8	<b>1.8</b>
AGITAN <sup>®</sup> 295	5.2	4.4
AGITAN <sup>®</sup> 655	15.3	3.1
AGITAN <sup>®</sup> 700	9.1	7.1
AGITAN <sup>®</sup> 760	<b>3.9</b>	2.8

**Table 3:** Influence of the type and quantity of emulsifier on the defoamer efficiency (values as air content in [%])

## 5.4 Influence of the dispersing agent

Wetting and dispersing agents play a crucial role for the foam behaviour of a paint formulation as they tend to stabilise foam due to their surfactant character. On the other hand they have an important influence on the release of air from pigments and fillers and therefore influence indirectly the efficiency of a defoamer.

The main properties of wetting and dispersing agents are the reduction of interfacial tension between the surface of pigments and fillers and the aqueous medium and the coverage of the pigment surface with dispersing agents. This results in the liberation of captured air in the void spaces of agglomerates and air bubbles which are adsorbed on the pigment surface. The more efficient the wetting of the pigment is, the more air will be liberated during the dispersion process. In combination with an efficient defoamer in this state of paint production an important content of air can be removed from the system. Inefficient wetting and dispersing agents will leave air on the pigments, which will be liberated in later stages of the production or storage of the finished paint.

In table 4 three high gloss paints containing TiO<sub>2</sub> are prepared with different dispersing and wetting agents but without defoamers. The properties of the paints are evaluated by visual inspection and by determination of the density. The absolute density is given as well as the relative density based on the completely defoamed, air-free reference system.

defoamer	polyacrylate	polyacrylate + nonionic wetting agent	polymeric dispersant
visual aspect	very foamy	foamy	foamless
density	d = 1.06 g/ml	d = 1.14 g/ml	d = 1.25 g/ml
relative density	d <sub>rel</sub> = 0.81	d <sub>rel</sub> = 0.902	d <sub>rel</sub> = 0.99
	air content [%]	air content [%]	air content [%]
AGITAN® 230	4.4	4.1	0.6
AGITAN® E 255	18.2	13.8	7.6
AGITAN® 650	5.9	4.7	3.1
AGITAN® 760	4.8	4.7	0.4
formulation type:	high gloss paint; carboxylated acrylic binder		
PVC:	15 %		
polymer content:	32 %		

**Table 4:** Influence of wetting and dispersing agents on the defoamer efficiency (values as air content in [%])

The visual aspect of the paint, which is prepared with a polyacrylate dispersing agent, is a very foamy condition after preparation. The measurement of the density and the comparison with the completely defoamed system confirms this impression.

If a wetting agent is added supplementary to the dispersing agent the foam after preparation is reduced, compared to the first measurement. This is again confirmed by the determined densities. The high performance polymeric dispersing agent leads to a nearly foamless paint in which 99% of the final foam free density is obtained.

The comparison reveals that the efficiency of the tested defoamers rises with the performance of the dispersing agent, independently from the nature and the initial efficiency of the defoamers. In the paint, which is prepared with the polyacrylate dispersant, the defoamers show only moderate efficiency. Three defoamers exhibit similar efficiency and only one is less efficient. In the classical combination of dispersant and wetting agent the results are similar to the anterior results.

In the paint which is prepared with the polymeric dispersing agent much lower air content values are found. The efficiency of two defoamers is much higher than the other defoamers, from which one shows regular and one less efficiency.

As displayed from these results the efficiency of defoamers can be increased in combination with a high performant dispersing agent. As a "side effect" much higher gloss values are obtained.

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