

## Defoamers



TEGO<sup>®</sup> Foamex

It is almost impossible to imagine industry today without surfactants. Their use is required in the most diverse processes to obtain a broad range of effects. Emulsifiers, for example, facilitate the incorporation of water-insoluble binders in waterborne paints. Other examples include additives which improve substrate wetting (see "Technical Background Substrate Wetting Additives") and dispersion of pigments (see "Technical Background Wetting and Dispersing Additives").

The most important property of these surfactants is their tendency to concentrate at interfaces such as the air/water boundary where they orientate according to their chemical structure.

Surfactants have an amphiphilic molecular structure. The hydrophilic area of the molecule penetrates into the polar liquid and the hydrophobic part into the gas phase. Consequently, the surfactant lowers the surface tension and stabilizes the system. However, undesirable side effects also occur: surfactants stabilize air, incorporated during manufacture or application of the coating in the form of foam, particularly in the case of waterborne formulations.

## What is foam?

Foam can be defined as a stable dispersion of gas bubbles in a liquid and is therefore a colloiddally dispersed system. In a paint formulation, the binder is the continuous phase. The dispersed phase consists of air or gas-filled bubbles.

If a stream of air is introduced into a liquid, the bubbles produced assume a spherical shape. As their density is less

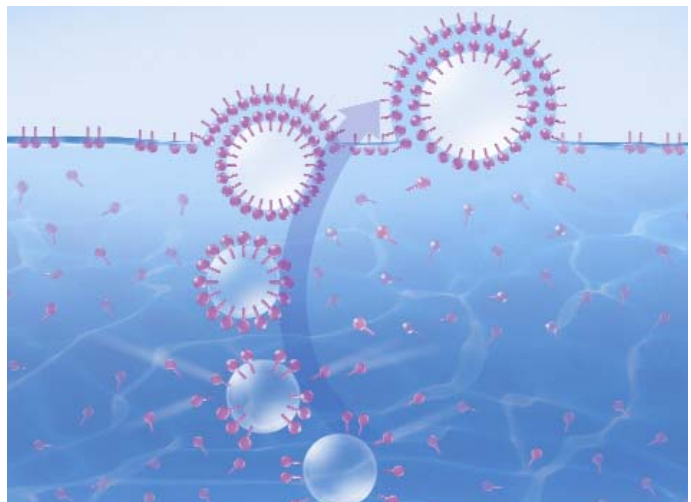
Figure 1:  
Rise and bursting of  
air bubbles in a  
surfactant-free liquid



than that of the liquid, they rise. When the individual bubbles reach and pass through a surfactant-free liquid, they burst. Air from the bubbles dissipates and the liquid previously surrounding them flows back. Pure, surfactant-free liquids do not foam (fig. 1).

In liquids containing surfactants, the unstable bubbles give rise to stable foam consisting of spherical bubbles. A surfactant film forms around the gas bubbles. If these bubbles reach the surface, which is also coated with surfactants, a lamella or double layer stabilized by the surfactant is formed (fig. 2).

Figure 2:  
Rise and stabilization  
of air bubbles in a  
liquid containing  
surfactant



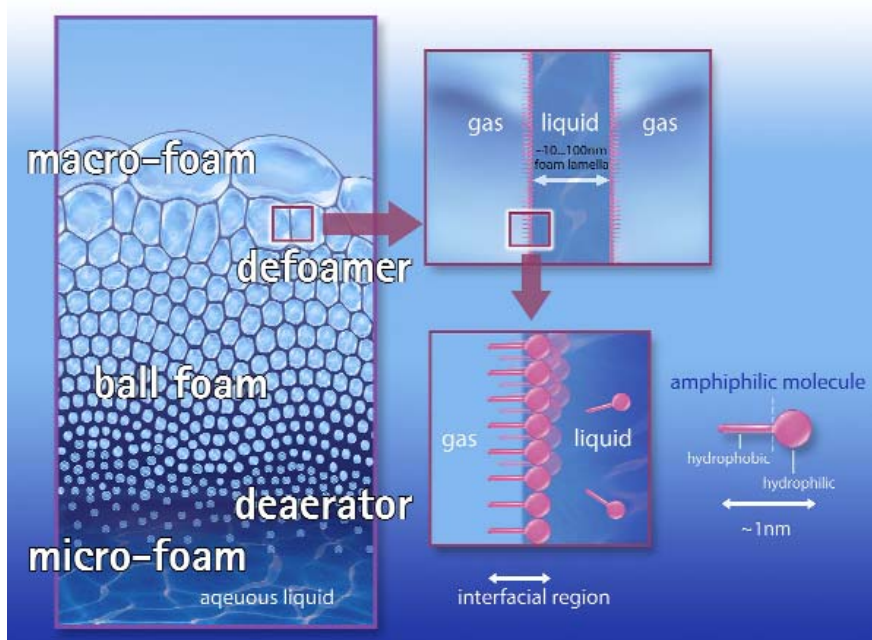


Figure 3: Detailed view on the liquid/air interface

As such double layer surface films can be several microns thick, this fine foam is very stable and extremely difficult to disrupt. The rising bubbles generally have a diameter greater than 50  $\mu\text{m}$  and give rise to macro-foam. Foam bubbles, which are so small that they rise only slowly, if at all, and cannot escape from the system, are termed micro-foam. The viscosity of the system plays a decisive role (see "Technical Background Deaerators").

The macro-foam bubbles, which have reached the liquid/air interface, retain their spherical shape as long as the air content is lower than that corresponding to maximum sphere packing density. Since in this phase of foam formation,

the volume content of the liquid is greater than that of the air, this foam is termed "wet foam". The subsequent bubbles cause a continuous rise in the foam head.

As the liquid flows out of the double layer under gravitational effects, the spherical foam is forced to take on another stable form: polyhedral foam. Polyhedral foam is called "dry foam" because it contains only a small amount of liquid. Because of the low film thickness of the lamella (approx. 100 nm), this foam is often relatively easily disrupted. The surfactant properties can lead to somewhat more stable foams. fig. 3 shows the described phenomena.

## Foam formation

Foam is produced during manufacture and application of waterborne coatings. Foam crown heads lengthen production times and reduce the effective volumes of production plants. Foam also interferes with the application process since it leaves various surface defects after drying. In printing, for example, foam impairs ink transfer and can also cause the ink reservoirs to overflow.

### How can foam be stabilized?

The following effects are involved:

- electrostatic repulsion of the treated surfaces
- steric effects
- surface effects such as the Gibbs-Marangoni effect which counteract stronger drainage of the lamella
- the Gibbs-Marangoni elasticity of the foam lamella

The Gibbs-Marangoni elasticity stabilizes foam because it increases the surface area when the foam lamella deforms. Consequently, the concentration of surfactant per unit area decreases and the surface tension increases proportionately which is energetically unfavorable. In trying to achieve the lowest possible surface tension, the stretched film contracts like an elastic skin. The foam bubble remains intact (fig. 4).

## How do defoamers work?

Current terminology distinguishes between defoamers and deaerators. In waterborne formulations, defoamers destroy the macro-foam on the surface and prevent large air entrapments. Deaerators evacuate the finely dispersed air out of the paint film as quickly as possible during application. In practice differentiation is not usually so clear cut. Thus defoamers are also effective to some extent against micro-foam. Both additives are active at the surfactant-stabilized air/liquid interface.

There is no single defoamer theory. Some explanations and prerequisites for effective defoamers are however known. Combating foam in waterborne coatings is described below.

A defoamer must exhibit a range of properties:

- insoluble in the formulation to be defoamed
- low surface tension
- positive penetration coefficient E
- positive spreading coefficient S
- dewetting mechanism

On the one hand, the active ingredient in the defoamer must be almost insoluble in the coating. On the other no defects such as craters should be generated. The defoamer must therefore be sufficiently compatible with the binder. Thus every defoamer is on a tightrope between compatibility and targeted incompatibility.

To develop its effect, the defoamer, emulsified into fine droplets, must penetrate into the foam lamella. Before the defoamer droplet can fully develop its positive penetration coefficient, the so-called pseudoemulsion film must be broken. This is formed as the defoamer droplets approach the foam surface with the formation of an asymmetric three phase film (oil/water/air).

The mathematical formula for the penetration coefficient shows that the required low surface tension of the active ingredient phase of the defoamer results in a positive penetration coefficient.

$$E = \gamma_{w/a} + \gamma_{w/o} - \gamma_{o/a}$$

$\gamma_{w/a}$  = surface tension of the foaming liquid

$\gamma_{w/o}$  = interfacial tension between the defoamer and the foaming liquid

$\gamma_{o/a}$  = surface tension of the defoamer

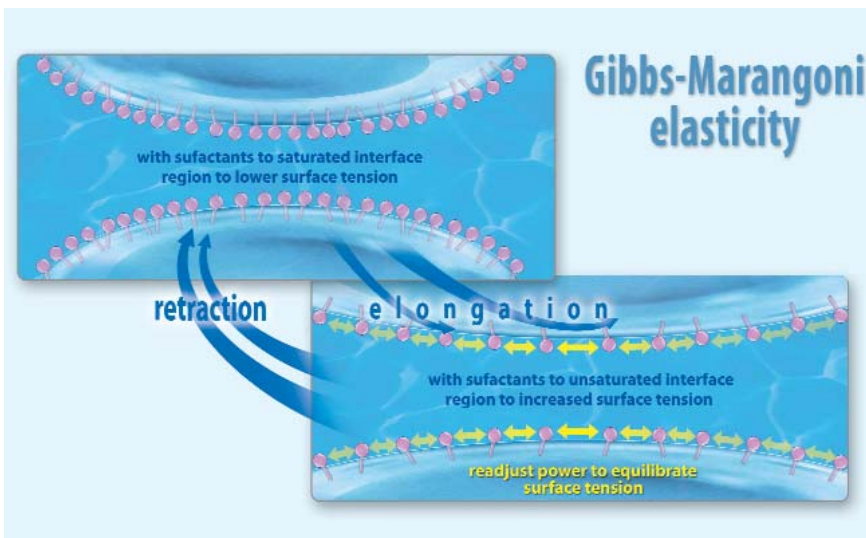


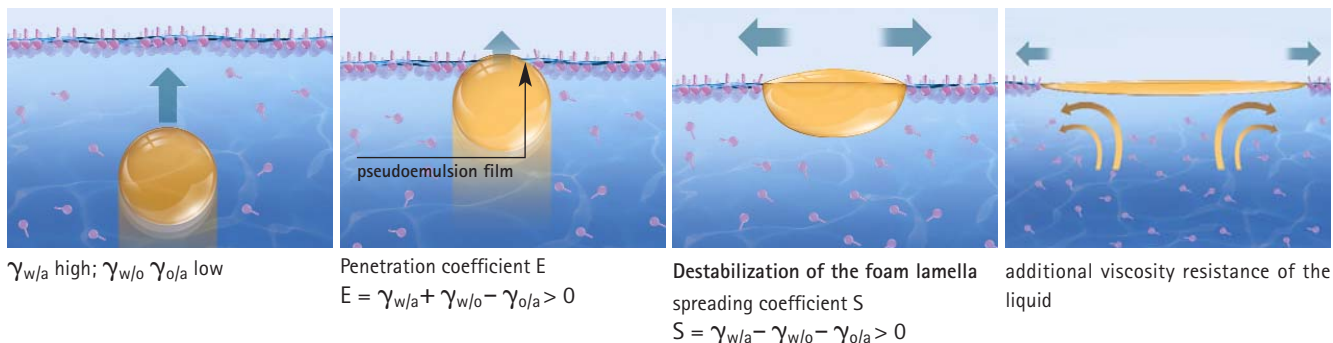
Figure 4: Gibbs-Marangoni elasticity

At the foam surface the defoamer droplets penetrate the surfactant film which stabilizes the lamella.

Because of its high spreading tendency, the defoamer droplet expands into a lens at the liquid/air interface. The spreading coefficient of the defoamer must be positive for this phenomenon to take place:

$$S = \gamma_{w/a} - \gamma_{w/o} - \gamma_{o/a}$$

Figure 5: Penetration and spreading of the active ingredient of the defoamer



The progressive spreading process reduces the thickness of the lens, the shape of which is altered by movements in the foam. Stresses occur until the lens breaks and the foam lamella ruptures. The resultant film is considerably less elastic than the surfactant film which previously stabilized the lamella. This destabilization facilitates rupture of the lamella (fig. 5).

The following mechanism is possible: The foam lamella thins through drainage (fig. 6a), so that the defoamer droplet can penetrate one side of the lamella (fig. 6b and 6c). Further drainage of the lamella liquid enables the defoamer droplet to then penetrate the other side of the lamella (fig. 6d). This process is termed film bridge forming (fig. 6e). Once this stage is reached, the foam lamella ruptures. The defoamer droplet is released and can become active again (fig. 6f).

The addition of finely divided hydrophobic particles, such as hydrophobic silica, increases the effect of defoaming substances. The reasons for this is as follows.

### Dewetting:

The hydrophobic solid aids piercing of the pseudoemulsion film. The surfactant film which stabilizes the foam lamella cannot wet the hydrophobic solid and "shrinks back". An unstable area results where the lamella is able to break (fig. 7).

### Which classes of substances have a defoaming effect in waterborne coatings?

Of the numerous defoaming formulations for waterborne coatings, those defoamers based on mineral oil and silicones are of greatest importance. Aromatic or aliphatic mineral oils have been

traditionally used as active spreading substances. Aromatic oils were used but entail physiological and ecological risks. Aliphatic oils are less toxic but their lack of compatibility in aqueous media often causes a serious reduction in the gloss of emulsion paints.

A highly effective class of defoamers is obtained by combining dimethylpolysiloxanes with hydrophobic and partially hydrophilic polyethers. This results in defoamers with very active spreading characteristics which are highly suited for use in modern waterborne coatings and printing inks. They do not impair

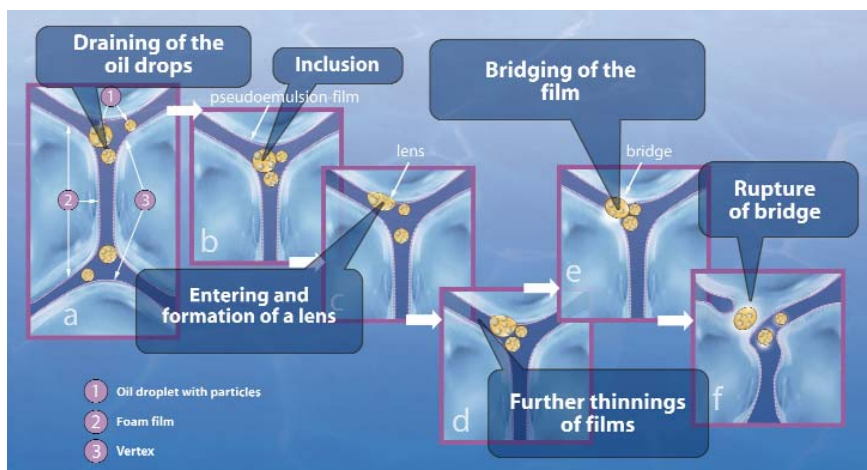


Figure 6: Film bridging during defoaming

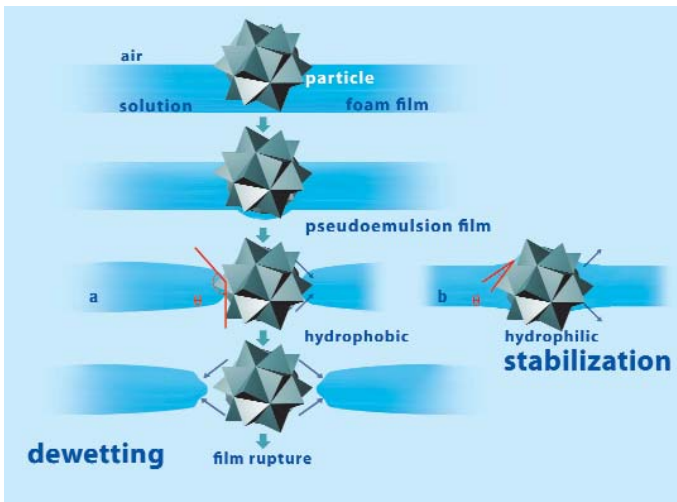


Figure 7:  
Dewetting during  
defoaming

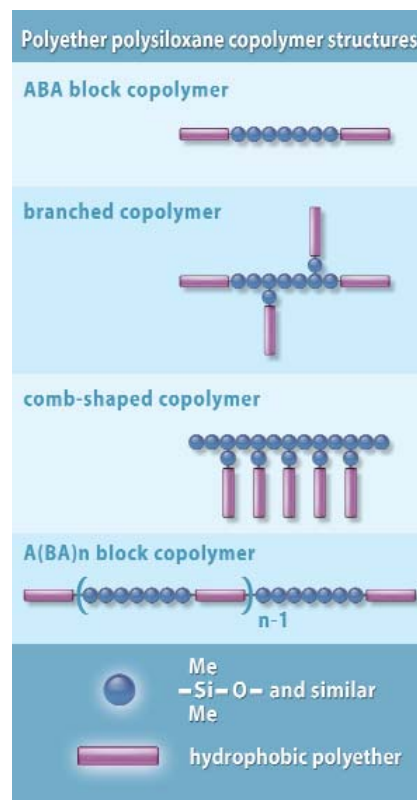
gloss and are highly compatible. Polyethersiloxanes are synthesized using SiOC- or Si-C linkages between polyether and siloxane blocks resulting in various possible structures (fig. 8).

Interfacial activity stems from the silicone block while the degree of compatibility is controlled largely by the polyether block. The choice of active ingredients is mainly dependent on the composition of the medium in which the defoamer must work. However, the complexity of paint formulations makes it difficult to explain clearly the relationships between the defoamer's structure and its property profile. Since very different requirements must be met, only general advice can be given; no universal solutions to these foam problems can be expected.

TEGO® Foamex 815 N, TEGO® Foamex 825 and TEGO® Foamex 855 are particularly effective in pure acrylic and styrene-acrylic systems. TEGO® Foamex 800, TEGO® Foamex 805 and TEGO® Foamex 822 are suited mainly for use in PU and PU/acrylic systems. Because of their high spreading force, some polyethersiloxanes are good defoamers even

without hydrophobic solids. TEGO® Foamex 805 and TEGO® Foamex 7447 are therefore supplied free of solids. TEGO® Foamex 845 has been developed specifically for hybrid systems (aqueous resin solution/emulsion blends) which

Figure 8: Typical polyethersiloxane structures



are particularly popular in printing inks and industrial coatings. This defoamer is highly effective in hybrid systems and resin solutions even after lengthy storage of the ink or coating.

### How are defoamers incorporated?

The dosage rate and effectiveness of a defoamer depend on the coating formulation, particularly the type of polymer dispersion, pH-value, degree of pigmentation, binder, etc. and the chemical structure of the additives used. Manufacturing and application processes also affect the type and amount of defoamer required.

When considering incorporation, a distinction should be made between defoamer emulsions and 100% active products. Emulsions such as TEGO® Foamex 800, 815 N, 822 and 825 do not pose a problem here as the ideal particle size distribution is specified. They can be added to the mill-base and require only homogeneous mixing in. Solids-free emulsions such as TEGO® Foamex 805 and 7447 can even be stirred into the finished paint.

With defoamer concentrates such as TEGO® Foamex 3062, 810 and 8050 the defoaming effect is largely determined by the method of incorporation, since it is at this stage that the particle size distribution, which governs effectiveness, is achieved. If the defoamer droplets are too small, insufficient mass is present to enable a lens consisting of active ingredient to be generated. Defoamer drops which are too large cannot penetrate the foam lamella and poor wetting results in the paint film (fig. 9).

Concentrates are therefore often used to defoam mill-bases. The defoamer is incorporated using high shear. Care must be taken that this is not excessive. The effect of the defoamer may be impaired by extreme shear forces or long stirring. The effectiveness of the defoamer is reduced, because too small droplets develop.

Low shear during addition may provide good results but often the defoamer shows incompatibility in the paint system. Thus bad wetting or irregular areas occur in the application.

Tego defoamers are designed to be used as supplied. If shear forces are inadequate during processing, then prior dilution of the 100% products (TEGO® Foamex 3062, TEGO® Foamex 810 and TEGO® Foamex 8050) with film forming aids or alcohol is recommended. Dilution in the range 1:1 to 1:9 facilitates incorporation into the batch and accelerates distribution in the formulation resulting in improved defoaming and a reduced tendency to cratering. The storage stability of prediluted solid-containing defoamers is generally limited and should be checked.

## Which practical tests are meaningful?

Defoamer performance must first be determined in the laboratory. Often it is not possible to transfer laboratory results to production scale without further testing. We are constantly striving to develop test methods which permit evaluation of the efficacy of defoamers under production and application conditions. The choice of test and any necessary modifications depend on the application method (brushing, spraying, dipping, printing, etc).

Many defoamers cause surface defects such as cratering which are just as undesirable as the problems caused by foam bubbles. These side effects must also be investigated using suitable tests.

### Stir tests

One of the methods used is a stir test which shows how much air is contained in the formulation as spherical bubbles.

### Flow test

The flow test permits evaluation of the effect and compatibility of a defoamer in a coatings formulation.

The procedure of both tests is shown in the Video "Defoamer test for polymer emulsions" on the enclosed CD-ROM.

Another stir test is used to determine the amount of macro-foam. Air is stirred into the medium to be defoamed under defined conditions and the resulting total volume including the foam head determined in a measuring cylinder (video "Defoamer test for printing inks and varnishes (stir test)"). This test provides information on the optimum operation of the mixing vessels if a ready made paint is used instead of a dispersion.

### Roller test

Because of the differing porosity and surface texture of the substrate (e.g. stone, wood, metal), foam development varies in intensity. On strongly textured surfaces, the amount of defoamer gauged as optimum by the stir test is not always sufficient to destroy foam occurring during application. The amount of defoamer needs to be adjusted to the application conditions.

The roller test reproduces real application conditions relatively closely so that it is possible to assess suitable concentrations of different foamers (see video "Defoamer test for emulsion paints" on the enclosed CD-ROM).

The above tests enable the most suitable defoamer and dosage to be ascertained for a given formulation, area of and conditions of application.

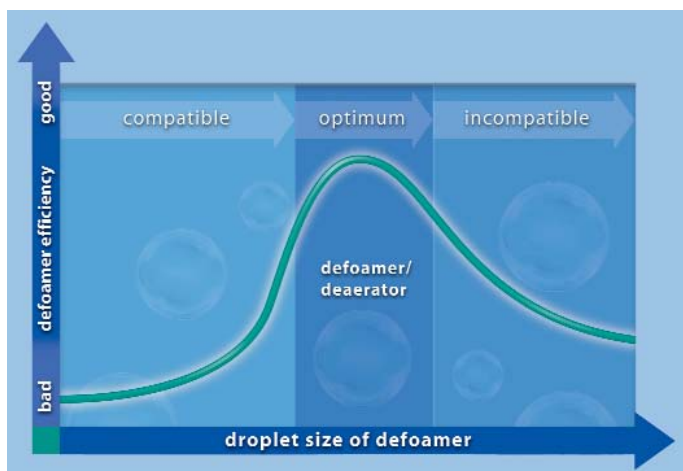


Figure 9:  
Effectiveness as a  
function of drop size



## FAQ:

*We use TEGO® Foamex 810 in a pigmented UV wood finish and sometimes have isolated craters in the product. We are unable to reproduce this defect in the laboratory. What can we do?*

We recommend diluting the defoamer with butyl glycol in a ratio of 1:1 (this does not apply to emulsions) or another glycoether before adding to the coating. Another possibility is to add one of our wetting agents. TEGO® Wet 270 in amounts of 0.1 to 0.4 % has proved very effective in such cases.

*We manufacture various interior paints. The PVC ranges from 50 % to 80 %. We also use various binders in these paints. At the moment we are also using various defoamers but should like to use just one. Is there a defoamer which is effective in all paints?*

No, even we have not found a universal defoamer. Emulsifiers and stabilizers used in the manufacture of emulsion

paints stabilize the foam and their huge variety is one of the reasons why there can be no universal defoamer.

TEGO® Foamex 855, however, exhibits a broad spectrum of activity. We have achieved good to very good results in various binders, such as styrene-acrylates or terpolymers and at various PVCs. Of course different amounts are required for different applications.

*Can defoamer emulsions be diluted with glycols such as butyl glycol to mix the defoamer into a parquet varnish without compatibility problems?*

No. You should not dilute with solvents such as glycols as they would destabilize the emulsion and certainly result in compatibility problems. Moreover, the defoamer droplets would be destroyed and the excellent defoaming action would no longer occur.

*How long does an aqueous dilution of a defoamer remain stable and how long can one use these diluted products?*

Diluted defoamer emulsions should be used within two days if they contain a solid (usually silica). Silica-free products such as TEGO® Foamex 805 can still be used even after storing for seven days. The diluted products should not be prepared with a solids content < 5 %.

*What types of pumps are suitable for conveying defoamer emulsions?*

Defoamer emulsions should, in principle, be conveyed with low-shear pumps, e.g. centrifugal pumps.