

# Foam

# generation, regulation, destruction testing and evaluation



# Foam Guideline TEGEWA working group "surface active substances" \*

#### \*Members

Dr. Britta Jakobs, Sasol Germany GmbH, 45764 Marl

Rolf-Dieter Kahl, BASF AG, 67056 Ludwigshafen

Drs. Hamke Meijer, Kao Chemicals GmbH, 46422 Emmerich

Dr. Dennis Miller, Clariant Produkte (Deutschland) GmbH, 65926 Frankfurt

Dr. Jörg Andreas Schröter, Ecogreen Oleochemicals GmbH, 06861 Dessau-Roßlau

Dr. Wolfgang Spiegler, BASF AG, 67056 Ludwigshafen (Chairman)

Dr. Rainer Traber, Ciba AG, CH-4002 Basel



# Contents

1.	Objectives of the brochure	4
2.	Theory	5
3.	Surfactants	10
Д	Defoamers	12
т. г		17
5.	Foam in practice	17
	5.1 High foaming systems	17
	Personal care cleansing liquids	18
	Hair setting foams	18
	Shaving creams	18
	Dishwashing liquids	19
	Hard surface foam cleaners	20
	Textile coatings	21
	Flotation	22
	Fire-fighting foams	23
	Foodstuffs	24
	5.2 Low foaming systems	24
	Household detergents	25
	Automatic dishwashing	26
	Industrial bottle washing	26
	Industrial and institutional cleaning	28
	5.3 Foam-free systems	29
	Fibre for paper	29
	Fibre from wood	29
	Fibre from waste paper	29
	Making the fibre suspension (pulp)	30
	Paper manufacture	30
	lextile pre-treatment	31
	Dyeing textiles	33
	lextile printing and finishing	34
	Metalworking	34
	Aqueous paints and coatings	35
	Sugar manufacture	36
6.	Foam test methods	37
7.	Literature	45
8.	Glossary	46

# 1. Objectives of the brochure

Foam plays an important role in many processes, both in industry and in the home. Sometimes foam is desirable and, indeed, a typical product characteristic; examples are shampoo and the head on beer. Often foam makes an important contribution to product performance, for example in washing and cleaning. On the other hand, in textile and paper manufacture, for example, foam disrupts the process and must therefore be prevented.

So depending on the application, foam must be specifically produced, regulated or destroyed and its properties fitted to the specific requirements. In many areas where surface activity plays a role, this opens possibilities for improved products and processes. Such developments require a basic understanding of the physical and molecular processes of foam formation and behaviour, a well as the ability to use laboratory methods for a realistic study of practical applications. The choice of appropriate test methods is of considerable importance.

Foam is a complex subject. This has led to development of an almost bewilderingly large number and variety of test methods. Different test methods may be difficult to compare, even though they often lead to similar conclusions. We think it would be useful to have a survey and comparison of the test methods used in the various applications.

Standardised test methods facilitate product testing in a well-defined way and efficient communication of the results throughout the relevant industries. Laboratory methods are continually being developed, in particular because of improvements in automation. The resulting need for further standardisation of test methods should be recognized, and acted on, at an early stage.

The object of this brochure is to treat the phenomenon of foam both from a theoretical and a practical point of view. For a variety of application areas it describes the requirements and shows how these are met. The brochure is aimed primarily at product developers and formulators working in the laboratory. It should also be useful for those designing and operating industrial processes where foam plays a role.

Following a theoretical introduction to foam, properties of both surfactants and defoamers are described. The application of such surface active substances plays an important role. They can be used for foam generation and control as well as to achieve specific foam properties.

Next, the many practical aspects of foam are described. There are strongly foaming systems, in which a special foam quality is needed, low foaming systems with a small, regulated foam volume and foam-free systems, in which foam is a nuisance and must be prevented or destroyed.

After a discussion of the general aspects of foam testing, the final chapter gives a summary of the test methods commonly used in individual applications. However, there are many other tests which are too specialised to be included in the brochure. In addition, we have only dealt with liquid foams, the emphasis being on aqueous systems, which are the most important ones in practice.



# 2. Foam: theory

# Introduction

Foam may be defined as a dispersion of gas in liquid, with most of the volume being gas. Foams are not thermodynamically stable and will gradually decay. The time scale over which this happens varies greatly. Transient foams stabilised by small surface active molecules decay in a few seconds. Foams stabilised by polymers or surfactants may persist for hours or even days. The majority of foams encountered in practice involve aqueous systems.

### Foam structure

There are two typical foam structures, which may be regarded as limiting cases. They are usually denoted by their German names:

#### Kugelschaum

The gas bubbles are spherical. This structure is typical for foams with high liquid content and is usually found shortly after foam formation.

#### Polyederschaum

Polyhedral gas bubbles are separated by thin liquid films. Three films meet at a line known as a Plateau border (after the Belgian physicist Joseph Plateau, 1801 - 1883). This structure, shown in Fig. 1, forms after the foam has drained. The liquid volume may become very low.



Fig. 1 Foam structure (Polyederschaum); picture: Clariant (Lab. Dr. Miller).

Foam drainage will cause a gradual transition from Kugelschaum to Polyederschaum. Fig. 2 shows the two structures in a foam column that has been draining. Drainage is slow with viscous liquids, which favours the Kugelschaum structure.



In a static foam column, drainage results in a decrease in the amount of liquid in the foam. At the same time the thin lamellae formed gradually rupture, so that the foam decays. The decay process thus involves a change in structure as well as a decrease in the foam volume.

Dynamic foam columns occur, for example, when foam is generated by air injection, circulation or continuous spraying. After a certain time a steady state is reached.

# Stabilisation and decay mechanisms

Pure liquids do not foam, because thin films cannot be stabilised without an adsorbed layer at the surface. A surface active agent, which need not, however, be a conventional surfactant is required to stabilise the foam. Depending on the type and concentration of stabiliser, the adsorbed layer may be mobile or immobile. Immobile layers, which are typically found with polymers, tend to give the more stable foams.

Fig. 2

6

Foam stability and decay are determined by a variety of mechanisms. Some of these apply to isolated thin films, whereas in others the junctions between films play an important role.

## a) Thin films

Stable foams can only form if thin films of the liquid are sufficiently stable against rupture. Such thin films may also occur on wire frames or as soap bubbles. There are several mechanisms by which they may be stabilised:

#### Gibbs-Marangoni Mechanism [1].

The film thickness may fluctuate. Consider a portion which has thinned as shown in Fig. 3.



The surfactant coverage of the interface is lowered, which increases surface tension. The surface tension gradient results in transport processes which repair the defect. An important aspect of this repair mechanism is that surfactant molecules moving into the thin spot will drag liquid with them. The Gibbs-Marangoni mechanism is most effective at intermediate surfactant concentrations. If there is too little surfactant present, the diffusion time is long and the interface is only partly covered. At high surfactant concentrations, adsorption from the bulk solution is fast and increases the surface coverage at the thin part of the film.

#### Surface viscosity

Intermolecular forces in adsorbed surfactant layers oppose movement of the molecules past each other. This results in a surface viscosity, which may be viewed as a two-dimensional analogue to the three-dimensional bulk viscosity.

#### Surface elasticity

When surfactant molecules have strong interactions, the corresponding films have not only a high surface viscosity but also strongly elastic



properties. Both effects lead to a stabilisation of the films and the related foam structures.

#### Steric and electrostatic repulsion

In ionic systems repulsions between electrical double layers contribute to the stability of the film. Steric interactions between bulky head groups (e.g. polyethylene oxide) or adsorbed polymers may also prevent the lamellae collapsing. Van der Waals forces act in the opposite direction, tending to destabilise the film.

#### Liquid microstructure

Fig. 4

At concentrations above the critical micelle concentration surfactants aggregate in the bulk phase. In thin films, liquid crystalline layer structures may occur [2]. These contribute to stability by slowing down film drainage.

### b) Foams

In a foam there are a variety of additional phenomena that can influence the stability.

#### Plateau border suction

Because of the curvature of the film at the Plateau borders, the pressure is lower than in the film. This is a consequence of the Laplace equation relating pressure, surface tension and curvature (Fig. 4). This figure shows a cross-section through a Plateau border. When applying the Laplace equation, it is important to note that in the Plateau border the radius of curvature is negative, because the surface is convex as seen from the liquid side. Liquid drains out of the film into the Plateau borders and the lamellae become progressively thinner. They may reach a metastable state where repulsion between the surfaces of the film, the disjoining pressure, balances the drainage forces [3]. Drainage in films is slowed down by high viscosity.



#### Mobile films

In mobile films thin spots can be formed which tend to move upwards, a phenomenon known as marginal regeneration.

#### Drainage due to gravity

Liquid flows downwards though the Plateau borders.

#### Solvent evaporation

Foams in open containers will slowly evaporate. This contributes to film thinning, especially at the top of the foam.

# Additional factors influencing foam formation and stability

When gas and liquid are mixed, bubbles are created, which are broken up by hydrodynamic forces. Foam will be formed if a stabiliser prevents rapid coalescence. The extent of foam generation will depend on the amount of gas that is mixed into the liquid and the mechanical stress (shear rate). With some test methods it is possible to vary these parameters systematically. In most cases, however, they are not welldefined, though qualitative differences are usually clear. It is therefore often difficult to compare foam generated by different methods.

Foam may also be made by nucleation of gas bubbles in a supersaturated liquid. This mechanism is particularly important for carbonated drinks.

As surface activity is required for foam stabilisation, one might expect lowering surface tension to be related to foaming. Although surface tension lowering is normally a requirement for foaming to occur, there is no general correlation between extent of foaming and static surface tension. As short time scales are involved, correlations are more likely with dynamic surface tension and this has been observed in some basic studies [4, 5].

#### Foam stabilisers

We can divide foam stabilisers into the following classes:

#### Small surface active molecules

Examples of this type of foamer are short chain alcohols and carboxylic acids. They give transient foams. Usually the foam stability goes through a maximum as the concentration increases. This can be explained in terms of the Gibbs-Marangoni mechanism.

#### Micelle-forming surfactants

Typical surfactants form stable foams. Foam lifetime increases with amount of surfactant, reaching a limit at high concentration.

Polymers

Polymers with amphiphilic properties can be very effective foam stabilisers. A well known example is beer, where proteins are responsible for the foam.

#### Partially miscible liquids

Surface activity is exhibited by liquid systems near a composition corresponding to phase separation. The tendency to foam will increase strongly on approaching the phase boundary.

#### Non-aqueous Foams

Non-aqueous foams may cause problems in distillation towers [6], oil production [7] and hydrocarbon fuels [8]. In some respects, the same principles apply to both aqueous and non-aqueous systems. Bulk and interfacial viscosity probably play an important role for hydrocarbon foams.



# 3. Surfactants

Surfactants have an important influence both on foam formation and foam characteristics. From a practical point of view, it is interesting to know which surfactant will give the right foam for a particular application. Some surfactant types are known to be strong foamers, others typically give low foam. The table below classifies the most important surfactant types as high, medium and low foamers.

	Surfactant type		Foaming
ANIONICS	Alkylbenzene sulphonates	high	
	Alcohol ether sulphates	high	Stable to hard water
	Alcohol sulphates	high	
	Alkane sulphonates	high	
	Isethionates	high	
	Olefin sulphonates	high	
	Sarcosinates	high	
	Soaps	high	Defoaming in hard water
	Alkyl ethercarboxylates	medium	Stable to hard water
	Sulphosuccinates	medium	
NONIONICS	Alkanolamides	high	Foam boosters
	Amine oxides	high	Foam boosters
	Fatty amine ethoxylates	high	Above cloud point: low foam- ing/defoaming. pH-dependent.
	Polyglucosides	high	Foam boosters
	Fatty alcohol ethoxylates	medium	Above cloud point: low foam- ing/defoaming
	Fatty alcohol mixed alkoxylates	low	Above cloud point: very low foaming/defoaming
	EO/PO copolymers	low	Above cloud point: very low foaming/defoaming
	Sorbitan esters	low	Suitable for food applications
CATIONICS	Di- and trialkyl ammonium salts	low	In general not stable
	Esterquats	medium/low	
AMPHOTERICS	Betaines	high	Foam less than anionics

The table is intended to show the typical properties of the various surfactant classes relative to each other. The structure of individual surfactants, for example length and branching of the alkyl chain, can have a large influence on the film stabilising and destabilising mechanisms (see sections 2 and 4) and hence on the foaming. It is therefore not possible to quote detailed foam properties applicable to a whole surfactant class. For example, amine oxides and alkyl polyglucosides with short C-Chains (< C10) foam less strongly than some alkyl ethoxylates. With longer C-chains, however, these surfactant types foam strongly and are used as foam boosters.

Correlations between chemical structure and foaming are confined to surfactants with the same structural type. This is illustrated by the following examples:

- With alkyl sulphates, foaming increases with C-chain length, reaching a maximum at about C16. Alkyl chain branching leads to a marked reduction in foaming.
- Foaming of alcohol ethoxylates depends strongly on the length of the polyethylene glycol (PEG) chain. Foaming is weak for short PEG chains and shows a strong increase when the PEG chain is long enough for the product to be water soluble. A further increase in the length of the PEG chain has only a small effect.
- Alcohol ethoxylates with short PEG chains contain some unreacted alcohol; this is a result of the production process. The content of free alcohol, which acts as a defoam-

er, is particularly high for products with low degree of ethoxylation and further reduces their tendency to foam.

- At similar HLB values, alcohol ethoxylates with longer C-chains give more stable foam. The foam volume, however, is usually smaller.
- On heating to above the cloud point, long C-chain surfactants show a more pronounced decrease in foaming than short C-chain ones.
- Surfactants based on short chain alcohols have faster dynamics. As a result, foam can be generated more quickly.
- With alcohol ethoxylates more branching of the alkyl chain leads to stronger foaming, and foam that is less easily destroyed.

In addition to these structure-activity relationships, the following relations between the physical properties of surfactants and their foam behaviour are of importance:

- Below the critical micelle concentration (cmc), the amount and stability of foam increases with concentration, reaching a plateau or a maximum near the cmc.
- The rate of foam generation also increases with surfactant concentration below the cmc. It correlates well with dynamic surface tension.
- In some systems, the effectiveness of nonionic foam boosters for anionic surfactants correlates with a lowering of the cmc [9].



- Soaps foam less with increasing water hardness. In hard water, they can act as defoamers due to the insoluble calcium salts formed.
- The solubility and, as a result the foaming behaviour, of nonionic surfactants is strongly temperature dependent. Above the cloud point alcohol ethoxylates are low foamers or even defoamers. This is caused by the phase separation into surfactant-rich phase and an aqueous phase with only small amounts of surfactant. The surfactant-rich phase forms small droplets (hence the turbidity), which, like oils act as a defoamer [10] (see section 4).
- Alcohol alkoxylates, such as EO-PO adducts, have a flatter cloud point curve than the corresponding ethoxylates. As a result they are poorer foamers or better defoamers [11].

In addition to the product classes mentioned above, there are a variety of commercially available special surfactants as well as many naturally occuring ones, some of which have important biological functions. These biosurfactants include, in particular, glycolipids, phospholipids (such as lecithin), lipoproteins (bile acids) and glycosides (saponin). In foodstuffs, fats and proteins are used as foam stabilisers (see section 5.1)

# 4. Defoamers

This section deals with all products that reduce foam, which for simplicity we refer to as "defoamers". Strictly speaking, one should distinguish between defoamers, which destroy foam present, and foam inhibitors, which prevent its formation. If the foaming is only to be reduced, but not completely prevented, one refers to foam regulators; these products can also be used to influence other foam properties.

Foam is stabilised by means of a dense and homogeneous film of surfactant on the liquid surface. Defoamers are effective when they can destroy this or prevent its formation. An efficient defoamer must therefore fulfil the following requirements:

- High surface activity, i.e. a stronger reduction of surface tension than the surfactant that causes the foam.
- At least partial insolubility in the foaming medium, otherwise it would act as a surfactant itself and contribute to foam formation or stabilisation.
- The drop or particle size should be similar to the thickness of the foam lamellae.



Hydrophobic oils, often in combination with finely dispersed hydrophobic solids, are used as defoamers for aqueous systems.

#### Oils

The defoaming action of hydrophobic oils is due to their surface activity and insolubility. This causes them to penetrate the water/air interface. The entry coefficient, E, which should be positive [12], is defined by the following equation [13]:

$$E = \gamma_s + \gamma_{se} - \gamma_e$$

 $\begin{array}{l} \gamma_{s} & = \mbox{Surface tension of the foaming liquid} \\ \gamma_{se} & = \mbox{Interfacial tension between foaming liquid} \\ & \mbox{and the defoamer} \end{array}$ 

 $\gamma_e\,$  = Surface tension of the defoamer

A large value of E is therefore favoured by a large surface tension of the foaming medium

and a large interfacial tension between foaming liquid and defoamer. A low surface tension of the defoamer will increase E.

As soon as the defoamer droplet has penetrated the interface, it begins to spread over it, provided the spreading coefficient, S, is positive.



 $\begin{array}{l} \gamma_{s} &= \text{Surface tension of the foaming liquid} \\ \gamma_{se} &= \text{Interfacial tension between foaming liquid} \\ & \text{and the defoamer} \end{array}$ 

 $\gamma_e$  = Surface tension of the defoamer

Due to the spreading of the hydrophobic oil, regions of the lamella are formed which are covered only by defoamer and not by surfactant. This causes destabilisation, and finally rupture, of the foam lamella.



Defoaming mechanism of hydrophobic oils

Fig. 5

13

- Defoamer must be insoluble in foaming medium
- Defoamer must have a low surface tension
- E > 0 (necessary)
- S > 0 (preferred)

The main defoaming oils are mineral oils, paraffin, fatty alcohols and their esters, fatty acids, and silicones.

Defoamers based on hydrophobic oils reduce the surface tension down to about 30 mN/m and have the advantage of good compatibility in aqueous systems. Silicone oils are polydimethylsiloxanes (PDMS), sometimes slightly modified, with a very low surface tension of about 21 mN/m. As a result they are highy efficient. However, they are generally incompatible with aqueous systems, which causes problems in many applications. To combine the compatibility of organic defoamers with the high efficiency of silicones, silicone oils are modified with suitable substituents. These organo-modified siloxanes are based on a silicone chain, which gives the required lowering of the surface tension.

#### Hydrophobic solids

Solid particles with suitable wetting properties also result in rupture of the foam lamellae. In commercial defoamers they are often used in combination with an oil. The effectiveness of the particles depends on the particle size, the hydrophobicity of their surface and the geometry. The thermodynamically favoured position of the hydrophobic particles is the liquid/air interface unless other effects stabilise dispersion within the liquid.

The interaction between hydrophobic solid and hydrophilic surfactant solution is an important aspect of defoaming. This interaction is described by the contact angle. A contact angle  $\phi > 90^{\circ}$  results in capilliary forces which cause liquid to flow away from the solid. The lamella becomes thinner until it no longer wets the particle [14] and then breaks (Fig. 6).





14

Defoamers that consist of hydrophobic oils and hydrophobic solids act by a combination of both mechanisms [15]. In addition synergistic effects may be observed. A possible explanation has been given by Kulkarni, Goddard and Kanner [16].



The basis oil first spreads over the foam lamella and thus enables the solid particles to come into contact with the surfactant molecules in the interface. Hydrophobic-hydrophobic interactions result in adsorption of surfactant on the solid. As a result, the amount of stabilising surfactant in the foam lamella is reduced and it ruptures.

Commonly used defoamers of this type are silicone compounds containing hydrophobic silicate particles, silicone oil (PMDS) and alkoxysiloxanes (silicone surfactants). In oil-based particulate defoamers the most important solid components are waxes, fatty acids, fatty acid esters, fatty alcohols and amides. The melting point of the particles must lie above the application temperature. Soaps, which have been used in detergents for many years, also have a defoaming action. This is caused by the formation of insoluble calcium soaps during the washing process and therefore depends on the water hardness and the builder system. Phosphate esters can defoam via a similar mechanism involving insoluble salts.

#### Surfactants

As already mentioned in section 3, nonionic surfactants foam very little above their cloud points and can sometimes be used as defoamers. The mechanism involves phase separation of the foaming solution when the temperature is above the cloud point. Examples of such defoamers, which in many cases also show good wetting, are EO/PO block polymers, alcohol alkoxylates and ethylene diamine EO/PO block polymers.

In general, two-component liquids with a partial miscibility region show increasing foamability on approaching the boundary where separation occurs. On entering the two-phase region, foaming is dramatically reduced. Two liquids in equilibrium are formed, the one with the lower surface tension acting as a defoamer [17].

The most important application areas of defoamers are described in section 5.3. The largest user is the pulp and paper industry. In textile production, defoamers of various types are used during dyeing of the fibres and textiles. Defoamers used in household detergents include fatty acids (soaps), phosphate esters, fatty acid esters, fatty amides, mineral oils, waxes and silicone compounds. Typical applications for surfactant defoamers are automatic dishwashing and sugar production.

# 5. Foam in practice

## 5.1 High foaming systems

Foam is desired and makes an important contribution to product properties.

Strongly foaming systems are of particular importance in the personal care area. Such applications include hair setting foams, shaving foams, soaps, shampoos, shower gels and bath products. Dishwashing liquids, foam cleaners and leather care foams are examples of strongly foaming household products. Important industrial applications include foam finishing for textile production, flotation and fire-fighting foams. Foams also play an important role in the food industry. A number of selected systems are described in this section.

#### Liquid personal care cleansing liquids

Products such as shampoos, liquid soaps, shower gels and bath additives should foam strongly. This is achieved by means of a suitable surfactant combination. The consumer associates foam with good cleansing and it helps making the use of the product a pleasant experience. At the same time, the foam reduces mechanical friction. In particular, creaminess and small bubble size give the impression of good skin care. Because of the larger surface, it is easier to foam shampoo on the hair than shower gel on the skin. Occasionally shampoos and shower gels are sold as aerosols which can be applied directly as foam from a dispenser.

A wide variety of suitable surfactants are available for personal care products. They enable the formulator to achieve the required foam properties. In addition, the toxicological and dermatological properties are of particular importance in personal care applications.

There are a large number of possible surfactants and combinations of them, as well as an enormous variety of personal care products. For this reason, we can only give general information on the surfactants used in this sector. A common base surfactant for liquid cleansers is the sodium salt of alkyl ether sulphate. This surfactant fulfils the requirements of ecological acceptability, high foaming and a favourable cost/performance ratio.

The foam of personal care cleansers can be described by the following terms:

coarse	stable	oily
fine	unstable	greasy
medium bubble size	milky	gelatinous
homogeneous	creamy	watery

Depending on the application, different types of foam are preferred. However, standardised test methods can seldom describe these differences in a way that is useful in practice. This is because both the amount of foam and its stability depend on the way it is produced, i.e. the mechanical action, as well as the type of soil and the water hardness. All these parameters vary considerably in personal care cleansing and cannot be properly simulated by standardi-



sed methods for measuring foaming and foam stability. For example, the mechanical action involved in washing ones hands is quite different from that involved in producing foam in a bathtub. Furthermore, the foam behaviour of surfactants can be strongly influenced by other components of the formulation. Thus care components, such as refatting agents or conditioners (e.g. quats) may cause a significant decrease in the amount and stability of the foam. Therefore during formulation development, foaming of the surfactants is normally tested in combination with other components that are likely to be present in the final formulation.

The foam properties mentioned above can normally be determined only visually or by sensory tests, in other words subjectively. The characterisation of individual surfactants by means of standard methods gives only an indication of their behaviour in practice. Tests for sensory and visual determination of foam are designed to be as close to consumer use as possible. This is normally done with in-house methods; these vary according to the developer and are not standardised. Companies are usually reluctant to publish these methods, which are an important part of their know-how.

A parameter of particular importance in the development of personal care cleansing formulations is the foaming rate. The washing procedure is simulated in a realistic and defined way using a panel test. The protocol describes the amount of product, the number of testers, water temperature, the nature and length of the washing procedure. The results, (amount of foam produced, foam characteristics, etc.) are also determined with a defined procedure. In order to get reliable results, the testers should be intensively trained and a standard formulation included in each test for comparison.

This type of test can also be used to determine initial foam generation of bath additives, when one takes into account that the mechanical action is different. Ideally the test is carried out in a bathtub under well-defined and realistic conditions.

#### Hair setting foam

Hair setting or styling foam is sold as pump or aerosol formulations, which produce a fine, creamy and stable foam when the product leaves the container. Unlike hair gels and hair sprays, this type of product is usually applied to the wet hair after shampooing. A hair dryer is then used to dry and set the hair. The elasticity of the foam can suggest different characteristics to the consumer: mild hair care or a high tech image.

Besides the cationic styling polymer, the main component of hair setting foam is surfactant. Often cationic surfactants are used because of their compatibility with the polymer. Additional components can be emulsifiers, thickeners, solvents such as alcohol, actives such as humectants, UV absorbers, etc.

#### Shaving foam

The main object of shaving foam is to soften the hair. This is achieved by the slightly basic pH of the soaps, which allows water to be taken up after the fatty sebum has been removed.



Softening the hair considerably reduces the force required to cut it, so that the shaving process is not perceived as unpleasant. An additional effect is to lubricate the skin, which reduces irritation.

Products for wet shaving may be formulated as solid soaps, pasty creams (both foaming and non-foaming), aerosol foams and aerosol gels. The following description is confined to foaming products.

The major components of a shaving soap, comprising about 65% of it, are sodium and potassium stearate. The main contribution to foaming is from the soft potassium soaps, which dissolve faster. Further typical components are coconut and palm seed oil, humectants (glycerine, propylene glycol), lanolin (for refatting and lubrication) and perfume oils. About 1-2 % free stearic acid is required to give skin compatibility to solid shaving soaps.

Aerosol shaving foams have become very popular. These products are modified shaving creams with propellant gases (propane, butane, isobutane) to generate foam. In the can, this mixture of soap and propellant gas is unstable and must therefore be shaken well before use. The addition of alcohol ethoxylates favours the stabilisation of the foam during use. The container is a two-component system, whereby one chamber contains the gel, a homogeneous mixture of soap and the "internal" propellant, and the other the "external" propellant. On opening the valve, this forces the gel out of the can. Non-foaming aerosol shaving foams are also modified soaps. Unlike the aerosol shaving foams they form a transparent, homogeneous mixture with the propellant. On opening the valve, a gel is obtained, which only foams once it is spread over the skin. The advantage of this type of product is that it does not have to be shaken before use. Shaving gels typically contain high molecular weight water-soluble polymers as thickeners.

#### **Dishwashing liquids**

In hand dishwashing, the cleaning effect is due to the effects of surfactants, in combination with mechanical and thermal energy. The dishes are cleaned in a 30 - 40 °C surfactant solution (washing liquor) by hand, using a sponge, cloth or brush. Afterwards the crockery is rinsed with water and put in a rack to dry.

The performance spectrum for a dishwashing liquid is complex. The primary requirements are cleaning and residue-free drying. Additionally, the product should disperse fat and other soils well, foam strongly, drain properly, be economical, have good skin compatibility even for sensitive persons and be toxicologically harmless. All organic components should have good biodegradability.

Though foam does not contribute to the cleaning process, it is important as an indicator for the state of the washing liquor. If the foam layer continually breaks, the liquid usually contains so much soil that it can no longer clean properly.

Typical compositions of conventional dishwashing liquids and concentrates are given in the following table.



Component	Conventional	Concentrate	Function
<ul> <li>Surfactants and cosurfactants</li> <li>Alkylbenzene sulphonates</li> <li>Fatty alcohol ether sulphates</li> <li>Fatty alcohol sulphates</li> <li>Fatty alcohol polyglycol ethers</li> <li>Alkyl polyglucosides</li> <li>N-Methylglucamide</li> <li>Alkylamine oxide</li> <li>Cocoamidopropyl betaine</li> </ul>	10-25 %	25-40 %	Wetting dishes and soil, removal of grease and other soil, foam generation and stabilisation
Refatter Fatty acid amides	0-2 %	0-3 %	Refatting the skin
Care components Protein hydrolysates Aloe vera	0-5 %	0-5 %	Skin care
Citric acid			pH regulation
Solubilisers Alcohols Cumene sulphonate Urea	0-7 %	0-10 %	Solubilisation
Fragrance	0-1 %	0-1 %	Aesthetics
Dyes	0-0,1 %	0-0,1 %	
Preservatives	0-0,1 %		Storage
Antibacterial actives Sodium benzoate	0-2 %	0-3 %	Bacterial control

#### Hard surface foam cleaners

Hard surface foam cleaners are strongly foaming, highly alkaline liquid products. They are used in the food industry, e.g. dairies and abattoirs, as well as in the home, for example as oven cleaners. In dairies and abattoirs, the cleaner is applied undiluted with a foam lance. Foam volume and stability are regulated via the air flow in the lance. Where the product can be used diluted (by a factor of up to 100) it is sprayed onto the soil. Then it is left to act for the required time and rinsed off with water.

Using a foam lance together with high pressure cleaning equipment results in a voluminous, clinging foam. It can remove recalcitrant soils such as dried blood, fat, protein and carbohy-



drate. This is used to clean the tiled walls or floors and stainless steel surfaces used in the food industry, for example in abattoirs, sausage factories, butchers' shops and dairies.

A typical foam cleaner can consist of the following: water, sodium or potassium hydroxide, sodium or potassium silicate, sodium or potassium pyrophosphate or tripolyphosphate, polymers (e.g. sodium polyacrylate), nonionic surfactants (e.g. C10 alcohol ethoxylate with 7-8 mol EO, or alkyl polyglucoside) and foam stabilisers (e.g. phosphate esters). If required, a solubiliser such as cumene sulphonate is included.

Burnt food remains in ovens are particularly difficult to remove; often this has to be done manually. Special cleaners are available to help. They are strongly alkaline sprays or gels suitable for removing incrusted fatty and caramelised deposits from ovens, cake tins, hobs, grills, saucepans and frying pans. These products can be used on stainless steel, glass and ceramics. The surfaces to be cleaned are sprayed and, after waiting for the recommended time, washed with a wet sponge or cloth.

These special cleaners usually contain anionic and nonionic surfactants (e.g. alkyl polyglucosides) to wet the surface and, in the case of sprays, as foamers. Alkalies such as potassium hydroxide and monoethanolamine or triethanolamine swell the burnt-on food remains and support the cleaning process. Further components are solvents such as glycol to increase soil removal, thickeners to improve adhesion to vertical surfaces and the underside of horizontal ones, propellants such as butane to generate foam, complexing agents and perfume.

In practical application tests, the most important parameters are drainage rate and foam stability. Foam stability and density are important for the cleaning power.

#### Textile coatings Carpets and thicker technical textiles

There are special requirements for carpets and technical textiles. Both often need to be coated with a polymer dispersion in order to function properly. Though foam is undesirable for some textile treatments (see section 5.3), in carpet coating the product is often "diluted with air", i.e. applied as a foam.

The coatings are predominantly aqueous with a solid content of about 50% and density of about 1000 g/L. They are foamed with an industrial mixer so that the density is typically about 500 g/L, though it may be as low as 100 g/L. Air is continually mixed into the polymer dispersion with a so-called mixing head via a rotorstator system. The polymer dispersions often contain solid fillers such as chalk or fire-retardants, so that foaming agents are required to help reach the required foam density. The dispersion or compound foam is applied with rollers (Kiss coater) or is applied directly the textile surface using a squeegee. After application the coating is either squeezed into the textile with a special roller system, or a second piece of textile is stuck to it (lamination).

The required foam properties vary. There is unstable foam (collapses immediately after app-



lication), metastable foam (collapses during drying) and stable foam (can still be recognized as foam after drying). Anionic or sometimes amphoteric surfactants are used to optimise the foam properties.

To test the foam, the polymer dispersion or compound is foamed with a kitchen mixer or a planetary stirrer. Then foam density and stability are determined. Defined criteria are used to describe the foam properties.

#### Non-woven fabrics

Aqueous binders (dispersions) may be used with Foulard and size presses or sprayed onto the fabrics. They can also be applied as foams to textile surfaces and non-woven fabrics. Vinyl acetate/ethylene, acrylate, PVC, polyurethane and styrol-butadiene dispersions are used.

The advantages of foam application are lower energy requirements for drying (air instead of water), a softer feel and the possibility of coating both sides. The foam is produced by mechanically stirring to entrap air, if required with the addition of surfactants.

The foams can be classified as unstable, metastable and stable. With unstable foams the density is about 30 g/L. Unstable foams give a very even application of the dispersion. For stable foams with a density of > 100 g/L additional foam stabilisers such as ammonium stearate are used. The formulation may also contain thickeners, fillers, and external cross-linkers. The foam viscosity plays an important role. Stable foams with high viscosity allow coating of the substrate without significant penetration. On the other hand, low viscosity products are suitable for impregnation.

Examples for the application of unstable foams are finishing of substrates by polymer coating (better grip, hydrophobisation, mechanical stability) and the toughening of non-wovens. Uses of metastable foam include easily cuttable fabrics and fire-resistant backings. Stable foams are used for black-out coatings of blinds, table cloths and coatings for windproofing or waterproofing.

#### Flotation

Flotation is the separation of suspended solids from a liquid by means of fine gas bubbles that rise to the surface. In practice it is mainly used for aqueous suspensions into which air is blown. Separation is based on the different surface properties of the solids to be separated, in particular their hydrophobicity.

In froth flotation, the gas bubbles adhere preferentially to the more hydrophobic components, so that these are carried to the surface. The hydrophilic components stay in suspension. The finely divided solid in the foam, which is usually the more valuable component, is separated and further refined.

In flotation, it is important that the foam can incorporate the solid particles well. These often stabilise the foam by collecting in the Plateau borders. However, the foam must not be too stable, as it should collapse after it has been separated from the liquid.

In naturally occuring systems, the differences in hydrophobic and hydrophilic properties are usu-



ally not sufficient for separation. The material to be separated is therefore made more hydrophobic by means of flotation auxiliaries known as collectors. The effectivity of a flotation process depends to a great extent on the selection of a suitable collector. These are mostly organic compounds or their salts. In ore and potash salt flotation, long chain amines are the most important products. Cellulose derivatives, starch, oils and petroleum are also used.

A second group of flotation auxiliaries are frothers. Nonionic surfactants with short alkyl chains are often used as frothers or foam stabilisers. Examples are C1-C10 alcohol ethoxylates or methylisobutyl carbinol. In practice many flotation auxiliaries show both foamer and collector behaviour.

Flotation was first used to separate lead and zinc ores. Later it was applied to other mining problems such as separation of sodium and potassium salts and also in the coal industry. Other uses are in wine production to remove suspended particles from the must, separation of industrial sludges resulting from precipitation processes and deinking in paper manufacture.

Surfactants influence the structure of both gas bubbles and foam. For practical tests, which take into account both effects, flotation cells are used. This enables large scale flotation to be simulated for process development and to solve specific technical problems.

#### **Fire-fighting foams**

To produce the foam, 0.1 - 6.0 % of a concentrate is added to the extinguishing water. The amount required depends on the type of con-

centrate, the material to be quenched and the fire-fighting equipment. The mixture is expanded together with air in a foam blower. The quality of the foam can be adjusted by varying the liquid/air ratio. A small amount of air leads to a heavy, "wet" foam. Light, "dry" foams are obtained by using a large amount of air. Whichever type is used, the foam volume is always many times larger than the water volume.

Fire-fighting foams have two main functions. The foam film cuts off the supply of oxygen from the air. In addition, foam cools the combustible material, thus preventing ignition or reignition.

For fires with non-polar liquids (oils and hydrocarbon fuels) fluorinated surfactants are used to produce the foam. An efficient, but ecologically preferable alternative, is to use a combination of natural protein (hydrolysed keratin) and fluoroprotein; this has become increasingly popular.

Fires of polar liquids (organic acids, alcohols, aldehydes and ketones) are more difficult to extinguish. These liquids are miscible with the foam and destroy it immediately. Special foamers are used for such fires. They contain gelling agents (polysaccharides). The first layer of foam collapses to form a floating, spongy film that protects the foam subsequently applied.

In addition to surfactants, the concentrates contain other components that improve their performance, e.g. anti-freeze, foam stabilisers and gelling agents. Various special standardised methods are used to test fire-fighting foams.



#### Foodstuffs

Foams can play a variety of roles in the food and beverage industries. Sometimes strong foaming is desired, whereas in other cases foam must be prevented as far as possible. In this section we will deal only with the cases where liquid foams are required.

Food foams generally consist of a liquid or solid dispersion medium in which a gas, usually air, is finely dispersed. The foam on beer, for example, has a low viscosity, whereas dough and parfaits are highly viscous or semi-solid. The many examples of food foams can be divided into two main types according to the type of stabiliser: protein or fat.

Protein stabilised foams, found typically in confectionaries, desserts and cream products, are usually stabilised with hen's egg-white. They are particularly stable, because the proteins are irreversibly denatured at the liquid/gas interface. This is not the case with proteins from milk, whey or duck's eggs.

In fat-stabilised food foams, such as ice creams, whipped cream or desserts, fat crystals hold the bubbles in place by forming a network around them. The relationships between the physical properties of the ingredients, mechanism of foam formation, optimisation of gas dispersion and foam stability are particularly complicated in these foams.

Mixed emulsifiers, which have both O/W and W/O properties, are often used to stabilise fatty foams. O/W emulsification facilitates the uptake of air during foaming whereas W/O

emulsification contributes to the stability of the fat crystal / water phase. Suitable emulsifiers are sorbitan ester derivatives, diacetyl tartrate esters, glycerine esters, modified triglycerides and saccharose esters.

Foamed foods, in particular confectionary and milk products, are very popular. Good foam stability is a general requirement. In addition, the consumer should be able to relate the sensory properties of the foam to its physical appearance. Small bubbles with a narrow size distribution generally give a light, fluffy texture and creamy sensation to the palate. Such products show good consumer acceptance. In addition to sensory tests, rheological measurments (flow curves) can be used to characterise these foams [18].

## 5.2 Low foaming systems

# Strong foaming is undesirable, the foam volume is regulated to a low level

Low foaming systems are of particular importance in washing and cleaning applications. In such cases, a certain amount of foam is acceptable, as it is a typical property of the surfactants which are required to give proper cleaning. As a result, the consumer often associates foaming with cleaning performance. In some cases, the product performance can actually be improved by altering the foam properties. Because of the different processes and application conditions, industrial and institutional cleaning (I&I) is considered separately.



#### Household detergents

Detergents are formulations that are used as aqueous solutions to wash textiles. The requirements include clean laundry, care of the textiles, skin compatibility, good environmental properties and low price. There are different applications: all-purpose detergents, colour care products, fine detergents and special detergents. The products may be sold as powders, liquids or gels. Modern detergents consist of 10 - 20 components, such as surfactants, builders, bleaches, enzymes and other additives.

Surfactants, which wash via their surface activity, are the basis of every detergent. They reduce the surface tension of water, so that the fibres are wetted better, and they help remove soil, in particular when it contains oils and fats. The surfactants used in detergents are mainly anionic and nonionic ones. The latter have the advantage of less sensitivity to water hardness. Cationics can improve performance when they are used together with anionic and nonionic surfactants. The action of the surfactant system depends on its composition and the interaction with the other components. In addition to these effects, foaming is a typical surfactant characteristic.

The volume and stability of the foam depend on many factors. This explains why surfactants and their mixtures can show very different properties. Anionic surfactants, in particular fatty alcohol ether sulphates, generally foam strongly. Nonionic surfactants tend to foam less. The intensity of foaming does not, however, indicate how well a detergent washes. Depending on the application, the foaming of a detergent is adjusted by the selection of surfactants and suitable auxiliaries.

- In all-purpose detergents low foaming surfactant systems are required for the 30 - 95 °C temperature range. This is achieved by addition of foam inhibitors such as silicone or paraffin oils.
- Detergents for woollens, on the other hand, need a stable foam with small bubbles to protect the fibres by reducing mechanical action. In this respect they are similar to shampoos and foam cleaners. These requirements are achieved by adding foam boosters, for example fatty acid ethanolamides, which increase the lamella elasticity.

Foam is still often erroneously seen as a requirement for good washing performance, for example in the case of detergents for washing by hand. In fact there should not be too much foam, as this dampens the mechanical action in the machine and makes the washing process less effective. Real problems are encountered when so much foam is produced that that it overflows from the machine.

As many surfactants have a strong tendency to foam, detergents include foam inhibitors or regulators. The best known foam inhibitor is soap - to be more precise, the insoluble calcium soaps formed in tap water. This mechanism only works if there are sufficient calcium ions present, which is not always the case in areas with soft water. Special silicone and paraffin oils are much more effective foam inhibitors for anionic and nonionic surfactants. Their action does not depend on water hardness (see section 4).

The usual test methods for the foaming of surfactants for household detergents are the perforated disc beating method, the turbine stirrer and circulation tests, as well as many in-house methods. To test the whole formulations, inhouse tests with washing machines are chiefly used.

#### Automatic dishwashing

The entire cleaning process in a household dishwasher consists of several stages or cycles with different functions. The dishwashing product is normally a system consisting of three components: cleaner, rinsing aid and a regenerating salt for the water softener in the machine. After each stage, the water is pumped off. About 10-15 % of the liquid then remains in the machine and is diluted by fresh water for the next stage. As a result, a small amount of the wash liquor remains in the machine until the final rinse cycle.

In the initial stage loosely bound soil is removed with cold water. The subsequent cleaning stage is a thorough application of hot wash liquor. A first rinsing step removes remaining soil particles that have attached themselves to the crockery and the surfaces of the machine. The hot rinse cycle and drying ensure that the crockery looks clean and dry at the end of the whole cycle. To achieve this a rinsing aid is required, even when the dishwasher has been optimised. The main function of the rinsing aid is to lower the surface tension of the water. The result is complete wetting of the crockery so that the rinse water runs off as a film. This type of drying is necessary to give the appearance of clean crockery that the consumer expects. All objects taken out of the machine should be dry and have a uniform shiny surface, with no spots or stripes.

Foam control is important for good cleaning. If there is too much foam, the mechanical action of the water jets is reduced. Large amounts of foam can prevent the sprayer from rotating properly.

The main cause of foaming in the dishwasher is protein in the soil, together with the mechanical action of the machine, which strongly promotes foaming. Therefore products for household dishwashers use only special low foaming surfactants. They regulate the foam instead of enhancing it. To give a further safety margin, defoamers are also used. In industrial dishwashing specially optimised wetter/defoamer combinations may be necessary to solve problems with persistent foam.

In addition to standard foam tests, methods are used which simulate the application. For example, dishwashers fitted with sensors are run with load of soiled dishes and cutlery similar to that found in practice.

#### Industrial bottle washing

Bottles of drinks such as beer, fruit juice, mineral water and milk are often recycled. They must be intensively cleaned before re-use. In



recent years there has been a strong increase in the number of recyclable plastic bottles (PET). This places special demands on the products and technology for bottle washing, because there are considerable differences between plastic and glass surfaces as regards structure and robustness.

Bottle cleaning is necessary for both aesthetic and hygienic reasons. Both factors must be taken into account. Cleaning the inside of the bottle is primarily a question of removing remains of drinks as well as soils, such as fungi, that have formed during storage of the empty bottle. The label and general dirt must be removed from the outside of the bottle.

All over the world, bottle washing is mainly performed as an industrial process. Special equipment is used, that normally requires highly alkaline cleaners. The alkali is added separately as part of an additive package, for example as 50% NaOH solution. In the cleaning process, the alkali concentration is 1 -2 % and makes an important contribution to the wetting and cleaning performance.

In addition to alkali, the formulations contain a special low-foaming surfactant system that is adjusted to fit the operating temperature. Endcapped alcohol alkoxylates are the main type used for this purpose. Typically, the surfactant concentration is 10 - 20 %. Other components are phosphoric acid (approx. 30 %) as builder and hydrotrope, gluconic acid (5-10%) or phosphates and complexing agents (1-5%) as softener and polycarboxylates (1-5%) as dispersing agents. Foam formation will depend on the equipment and details of the process and may cause considerable problems. In particularly critical cases, it can cause the bath to overflow and the remains of labels prevent jets, pumps and heat exchangers from working properly. The foaming tendency of alkaline baths generally increases with age and the number of bottles that have been cleaned. There may be big differences in foaming, depending on the type of bottles, the machine and cleaning rate.

Foam formation is caused by substances that have become entrapped in wash liquor or formed in it. These are, for example, pigments and glue from the labels or chain lubricants. Also, drink remains are a source of substances that form or stabilise foam. Thus remains of beer, oil, lemonade, fruit juice or milk tend to foam, because they contain foam active components such as sugar, starch, protein, pectine and their degradation products, as well as saponifiable oils and fats.

Foam formation results from the mechanical effects of the cleaning equipment, i.e. from pumping, splashing and spraying. The alkali concentration of the cleaning bath is of particular importance for the foam behaviour. In foam regulation, the different effects of foam formers and foam stabilisers must be considered. The majority of defoamers used in other technical areas are not used in bottle cleaning, because they are either unstable in the wash liquor, insoluble in cold water or not permitted for food applications.



The test methods used simulate both mechanical action and the composition of the wash liquor, so as to be as close to practical applications as possible. Foam is generated by pumping or by spraying the test liquid onto a surface of the bulk liquid with sufficient mechanical energy and entrained air. The test liquid is designed so that it contains the most important foaming components that can occur in practice. Simulation of the process occurs by varying the pump speed, the height from which liquid falls, the temperature and the jet diameter. A common method is the circulation test.

#### Industrial and institutional cleaning

There is a wide range of application of industrial and institutional (I&I) cleaners. This sector includes cleaning kitchens in hotels, hospitals and cantines, commercial cleaning, treatment of metal surfaces and car washing. Cases where foam plays an important role, some of which are dealt with in other sections of the brochure, are in particular:

- Cleaners for dairies, butchers' shops and bakeries
- Cleaners for bottle washing or process equipment such as tanks and pipes
- Laundry detergents for hotels, restaurants and health care (doctors surgeries, hospitals, retirement homes)
- Dishwashing products for restaurants, bars, cantines and hospitals

- Hard surface cleaners for floors, buildings, outside walls, windows and general purpose use
- Cleaners for the transport sector, private cars, lorries, public transport, trains and rails, aeroplanes and ships
- Metalworking, i.e. cleaning and de-fatting surfaces, for example in the galvanic industry

Cleaning in the I&I sector is mostly done by trained personnel using special machines. The use of machines makes careful control of foaming especially important. Two cases may be distinguished:

- Foam is intentionally produced and regulated during the process, e.g. in carpet cleaning. The foam is used to disperse the soil.
- Foam must be eliminated as far as possible as it is a major problem. This is in particular the case for spray cleaning applications; the high energy causes strong foaming which leads to a much lower cleaning performance. Foam is also a nuisance if a good liquid runoff without residual droplets is required.

Foam stabilisation is caused by both the surfactant mixture and the soil. Both synthetic polymers and natural ones, such as proteins, have a particular tendency to stabilise foam. The cleaner is normally formulated to give an optimum combination of de-fatting, emulsification, soil dispersion and foaming properties. The nature and amounts of natural foamers, on the other hand, are often unpredictable. Other parameters such as temperature, pH and electrolyte concentration also influence foaming. This results in stringent requirements for the surfactants and defoamers in the formulation. Both in-house methods and the common standard tests are used to investigate foam for the development of surfactants and formulations.

# 5.3 Foam-free systems

# Foam is not wanted and should be avoided or destroyed

In many industrial processes formation of too much foam can cause difficulties and even force the process to be stopped or give rise to unacceptable product properties. In these cases, foam must be effectively and reliably reduced to a minimum. The cause of the unwanted foam is either surface active substances in the raw materials or surfactants that are required in the process itself or in previous steps. The quality and source of the raw materials can affect the type and amount of surface active substances contained. Paper and fibre manufacture, textile pre-treatment, textile printing and finishing, metalworking, aqueous lacquers and sugar production are examples of foam-free processes and are described in the rest of this section.

#### Fibre for paper

Paper fibre is the raw material for paper and cardboard. It is freshly produced from wood or obtained from waste paper. For paper and cardboard production it is made into a suspension, the pulp. Foam occurs in the steps where surfactants are added or surface active substances formed and air introduced into the suspension.

#### Fibre from wood

The fibres are stuck together by lignin. The digestion of the raw fibre consists of destroying the lignin as far as possible. This is done either mechanically, forming mechanical pulp or chemically to give chemical wood pulp. In the chemical sulphate-cellulose process, surface active sulphonated lignin is formed. Together with other organic compounds it can enter the cellulose waste lye and cause foam problems.

Resin is removed from the wood by boiling the chippings in a strongly alkaline solution. This transforms the saponifiable resins to strongly foaming fatty acid soaps and resin soaps. Surfactants are added to improve the wetting properties of the alkaline solution. They are also required to emulsify or disperse the saponified and non-saponified resins so that they can be removed more easily.

#### Fibre from waste paper

Waste paper is disintegrated by mixing with water in a rotating drum. This separates the fibres and removes coarse impurities. The subsequent "deinking" removes the major part of the print. Deinking is a flotation process in which foam is intentionally generated (see section 5.1).

In the flotation process, air is blown into the suspension of the waste paper in hard water. Without additives, the bubbles do not adhere



strongly enough to the printing ink particles to carry them to the surface. Therefore sodium soaps (or other surfactants) are added. The hydrocarbon chains of the sodium soaps attach themselves to the ink particles so that the hydrophilic heads point outwards. The calcium ions in the hard water displace the sodium ions and a sticky hydrophobic layer of calcium soap forms round the ink particle. This enables the particles to attach themselves to the bubbles, so that they rise to the surface where they form a stable foam on the surface. This foam is removed mechanically or by overflowing.

High turbulence on air injection favours formation of small bubbles, which are better at collecting ink particles. On the other hand increasing the turbulence makes it more likely that particles already on bubbles become detached. The process is optimised by suitable construction of the flotation equipment and choice of additives.

#### Making the fibre suspension (pulp)

After preparation, the suspension is diluted and mixed with further raw materials, fillers and auxiliaries. Modern plants use continuous mixing with pumps and stirrers. Pumps mix very effectively, when different liquids are sucked in together. The pumps and stirrers should be designed to avoid entraining air, in order to prevent foam formation.

Foam properties depend mainly on which type of wood is used. Pine woods give strong foaming on the surface, due to the sulphonated lignin. Wood from deciduous trees gives a more viscous foam that is stabilised by polyhydroxyaldehydes (sugars) as well as sulphonated lignin. Typical defoamers are formulations of mineral oil with N, N'-ethylene bisstearamide, silicone oils and alcohol alkoxylates. Their effectiveness is tested with the usual standard methods.

#### Paper manufacture

Paper is a matted sheet of natural fibres. It is made by placing an aqueous suspension of fibres and auxiliaries on a sieve, draining and pressing. The surface is then refined by sizing and coating. The individual steps of paper manufacture, starting from the suspension (pulp) are:

- stock preparation at the headbox
- forming a sheet
- pressing and drying
- refining the surface

In the first three steps the fibre suspension is evenly distributed over the rotating sieve of the paper machine, and then water is removed so as to form a sheet. The paper is made denser by pressing perpendicularly to the sheet surface. Heating increases the dry content from a maximum of 55 % after pressing to 94 %. Air in the fibre suspension makes the sheet uneven and must therefore be removed. This can be done by means of mechanical/thermal deaeration. Alternatively defoamers or deaeraters can be added.

The foam on the water passing through the sieve is stabilised by surfactants. It contains between 0.5 and 5 % air. Alcohol alkoxylates and their mixtures with paraffin oil are used as defoamers. A suitable test is measuring the



foam value in the paper pulp by compression. In more practically oriented systems this is done by means of a foam channel.

Entrained air that becomes trapped in the paper pulp and in white water is stabilised by fibres, hemicellulose and fillers. The liquid has a high surface tension (approx. 65 mN/m) and contains between 0.5 and 5 % air by volume. For this application fatty alcohol dispersions are used as defoamers/deaeraters. A typical composition is 27% long chain fatty alcohol (C20 and longer), 1.5 % PEG 6000, 1.5 % Tween 20 and 70 % water. The performance of the deaerater is tested by means of an ultrasonic technique in which the frequency measured increases with the volume of entrapped air.

There are two types of surface finishing: sizing and coating. Sizing involves application of auxiliaries such as starch and latex in order to control the moisture uptake of the paper and improve the dimensional stability. When paper is coated, a layer of pigments, binders and auxiliaries is applied, so as to smooth the surface and make it easier to print.

There may be foam problems in coating production when the mixture of pigments, binders and auxiliaries is pumped or sieved. These are best solved by reducing air entrainment. Defoamers may also be used, but have only a limited effect due to the high viscosity of the coating. Fatty alcohol alkoxylates and their mixtures with paraffin and silicone oils are used for this purpose.

The foam consists of the coating mixture with 0.2 - 5 % entrapped air. For this type of foam,

density measurement, for example with a pycnometer, is used as a test.

#### Textile pre-treatment

The object of pre-treating the raw product (woven or knitted textile) is to enable good quality dying, printing or finishing. It is performed in several steps: singeing, desizing, boiling off, bleaching and optical brightening, mercerisation and laugieren. Apart from singeing, these are all aqueous processes, in which dry or moist textile is immersed in, or sprayed with, a solution of chemicals. In the pre-treatment processes, as well as in the subsequent dyeing, printing and finishing, air can enter the liquid due to turbulence or via the textile itself. The bubbles are stabilised by surface active substances, resulting in foam. Measures taken to suppress or destroy the foam and to deaerate the liquid depend on the machines and processes involved.

In the pad method, the pre-treatment liquor is in a tapered piece of cloth (gusset) between two rubber rollers. The textile web is made to go through the gusset and pressed to give the required moist weight (residual moisture). In this way the textile is impregnated with the liquid. Foam and deaeration do not present a great problem in this case. The liquor is pressed into the fibre mat by the rollers and it mechanically displaces the air.

In the exhaust method, the textile, thread or thread package is immersed in the pre-treatment liquor. The chemicals diffuse to the fibre and adsorb onto it. Microdispersed air bubbles stick to the hydrophobic fibre and must be dis-



placed by addition of a deaerater. Bubbles in the packages not only prevent uniform adsorption of the dye, but form foam aggregates which disrupt the circulation of the liquor.

An additional foam problem in the exhaust process is floating foam. This can be due to strong circulation of the liquor (jet process) or the movement of the textile web or yarn (jigger and winchbeck) which lead to turbulence. The foam can cause the textile to float so that it does not move through the bath properly. It must be avoided as it results in non-uniform colour (e.g. stress marks and folding lines).

The mechanical entrainment of air, and hence the foam problems, are greatest in the discontinuous systems (jet, jigger, winchbeck). The strong turbulence in the jet can even result in sufficiently high shear rates to destroy the defoamer emulsions, so that they stop working after a time. Turbulence can be minimised in both discontinuous processes and the semi-discontinuous ones (pad batch, pad roll) by suitably guiding the material. However, air entainment via the textile itself cannot be avoided.

The *desizing* step removes sizing agents that were applied to reduce abrasion during weaving. The desizing liquor may be enzymatic (for starch) or alkaline (for synthetic sizing agents). In order to reduce foam problems, surface active substances are added as wetting agents. They allow the liquor to penetrate the textile. Silicones are the usual defoamers. In enzymatic desizing alcohol alkoxylates and phosphate esters are also used. In the *boiling off* step raw cotton is boiled under strongly alkaline conditions with the addition of wetting agents, detergents and complexing agents. A large number of substances in or attached to the fibre are removed, e.g. hemicelluloses, lignins, pectines, fats, waxes, watersoluble natural dyes and seed husks. The process improves the absorbency of the textile. With the usual process chemicals little or no foam develops in the liquor. Foaming is prevented by the use of alcohol ethoxylates with low cloud points or by end-capped alcohol alkoxylates.

In *bleaching and optical brightening* wetting agents and stabilisers for hydrogen peroxide cause foam. The defoamers used must be stable to oxidation. In cold pad batch bleaching and pad batch oxidative treatment, alcohol alkoxylates and phosphate esters are used to control foam. Defoamers based on organic esters are used in chlorite bleaching.

*Mercerisation* is the treatment of cellulose fibres with concentrated NaOH (up to 30 %) in a mercerising machine. The process gives the fibre high gloss and improves uptake of dyes. In laugieren the textile is treated with sodium hydroxide (15-30 °B at 10-20°C) without mechanical tension; it is performed with a padder together with a roller system for lateral stretching. At these high alkali concentrations and liquor viscosities, alcohol sulphates are used as wetting agents and phosphate esters, for example tributyl phosphate, as defoamers.

In the laboratory, the perforated disc beating method gives a good simulation of foam caused



by textile entering the liquid in a jigger, or hitting its surface in a winchbeck. To test deaeraters there are various in-house methods. One such method involves putting a winding spool with hydrophobic raw cotton yarn in a measuring cylinder containing the pre-treament liquor. The liquid level rises at first and then sinks as air is displaced from the winding spool. A deaerater is more efficient, the faster the liquid level sinks and more effective, the lower the final level.

#### **Dyeing textiles**

Dyeing textiles includes the following steps: colouring by the dye adsorbing onto or entering the fibre, fixing it and washing to remove dye that has not been adsorbed or fixed. The processes and equipment are similar to those described in the section on textile pre-treatment.

In dyeing, as in textile pre-treatment, one distinguishes between pad and exhaust processes. In the pad process the textile is first impregnated with dye in the padder. Then the dye is fixed in a second process by storage (pad batch and pad roll), steaming (pad steam) or dry heat (pad dry). In the exhaust process, the textile is immersed in the bath either continuously (liquor processes) or repeatedly (jigger and winchbeck). Alternatively it may be sprayed (jet dyeing). Air entrainment occurs by the same mechanism as in textile pre-treatment and is stabilised by the dyeing auxiliaries such as wetting, smoothing and dispersing agents.

For foam control the chemicals are selected to be low-foaming and defoamers are also used. Generally a temperature programme is used in dyeing. Starting at room temperature, the temperature is gradually raised, e.g. to 130 °C in polyester HT-dyeing under pressure. The temperature remains constant for a certain time and is then lowered. Defoamers must be effective over the whole temperature range.

In the padder processes (pad batch, pad roll and thermosol) deaeraters are based on alkylarylpolyglycol ether sulphates, phosphate esters, alkohol ethoxylates and mineral oil emulsions. In the exhaust processes with the vat, jet or jigger, typical deaeraters are phosphate esters, alcohol alkoxylates and mineral oil emulsions; in difficult cases silicone oil emulsions are used. In the high temperature processes in the jet, mineral oils, carboxylic acid esters, silicone oils and phosphate esters are found to be very efficient without causing problems for the process.

When carpets are dyed or printed, the high volume of the fibres brings a great deal of air into the liquid and traps it. Products with deaerating properties are used to help remove the air. In order to prevent patches of different colour intensity, the defoamer/deaerater must be easily dispersible and have high stability in the dyeing liquor. Silicone defoamers cannot be used because they can result in silicone stains and can cause problems with the fireproofing. In general, the defoamers used are based on mineral oil and alcohol alkoxylates.

Investigations of foaming and the action of defoamers are often carried out in a laboratory jet apparatus. The TEGEWA working group "dyeing auxiliaries" has carried out many round



robin tests, but reproducibility has been poor with agreement only on general trends. Nevertheless, this group has concluded that simulation of high temperature (HT) dyeing in a laboratory jet apparatus can give a comparison and evaluation of defoamers [19]. Foam formation and defoaming in the jet, including the temperature influence, can be simulated very well with the circulation test.

#### Textile printing and finishing

The final steps of textile treatment are printing and finishing. Printing is colouring particular places to give a pattern or picture. There are various printing processes: roller, flat screen, rotary screen, transfer and ink-jet. Normally these techniques all involve the same sequence of operations: printing, steaming and washing out.

When the printing paste is made, stirring and homogenisation can cause air to become entrapped. Bubbles in the paste result in pale spots on the textile and must be removed by the use of defoamers/deaeraters. These are usually based on phosphate esters, long-chain organic esters and mineral oil emulsions.

In finishing, the coloured or printed textile is given additional properties by application of effect chemicals. Hydrophilising agents give a soft feel whereas hydrophobising agents are used to repel water and soil. Additional additives are antimicrobial and antistatic agents as well as flame retardants. UV absorbers are used in order to protect the textile from ultraviolet radiation. Finishing, involves very similar processes to pre-treatment and gives the same foam problems. In general, the test methods and defoamer types used those described in the section on dyeing. If plasticisers such as quaternary ammonium compounds or polyethylene/acrylic resin emulsions are used in finishing, foam can occur when the liquid is vigorously circulated. Silicone defoamers and mineral oil emulsions are used to control this. Foam can form when finishing with antistatic agents because of the low surface tension and hydrophobic properties of these products. For this application phosphate ester defoamers are very effective and do not interfere with the process.

#### Metalworking

Most metalworking operations require lubrication and cooling. This is achieved through the use of special fluids. The composition of the fluids varies considerably according to the individual process.

Important formulation types are:

- O/W emulsions. By using an emulsion, the lubrication properties of oil can be combined with the cooling effect of water. The formulation contains an emulsifier.
- Aqueous solutions containing corrosion inhibitors and polyalkylene glycols or their derivatives.

The fluids contain a variety of additives to optimise corrosion inhibition, improve lubrication and wetting, prevent growth of bacteria and control foam.



Metalworking generally involves high shear, and is therefore very conducive to foam formation. Foaming is undesirable as it reduces cooling and lubrication. Also it makes it difficult for the operator to see his work. Build-up of foam in the circulation system can also cause problems. Formulation of metalworking fluids therefore requires combining good emulsification and/or wetting properties with a very low tendency to foam. This is achieved by selecting the formulation components (in particular emulsifiers and wetting agents) so as to minimise foaming. The foam can then be further reduced by adding small amounts of defoamer.

Defoamers tend to lose their performance over a period of time, because they are removed by flotation or by the filters used to clean the circulating liquid. Reducing these effects is an important aspect of defoamer selection.

Aeration, the trapping of small air bubbles in the liquid, is related to foam formation. Metalworking fluids should be optimised for both defoaming and deaeration.

Users and formulators of metalworking fluids use a variety of tests. For general development work, the following methods are suitable:

Shaking tests. Such tests have the advantage of speed and simplicity, but do not simulate metalworking operations. This method is widely used and experienced operators can give a good estimate of the foaming behaviour in practice. An example of a suitable shaking test may be found in ASTM D 3601.

- Blender tests. The fluid is agitated with a laboratory blender. Sometimes air is also bubbled through it. The high shear used makes this test appropriate for metalworking applications. American norm ASTM D 3519 describes a blender test.
- Circulation Test. Foam build-up is simulated. A normed version has been published in DIN EN 14371.

In the metalworking industry, standard test methods are usually adapted to correspond better to individual conditions encountered in practice [20]. Solutions should be allowed to age for at least one hour so that the mixture can equilibrate, for example via anionic surfactants reacting with water hardness.

#### Aqueous paints and coatings

For aqueous coatings, two distinct properties of defoamers are important: defoaming itself and deaerating. Macroscopic foam formed on the surface of the coating after application must be destroyed (defoaming). Also air trapped during the coating process must be removed (deaerating). The latter is referred to as "microfoam". Commonly used defoamers always help prevent the formation of microfoam.

In addition, defoamers for coatings need to be compatible with the binder. An important requirement is that they must help prevent the formation of surface irregularities (crater defects). The defoamer is normally hydrophobic, spreads easily over interfaces, has a low surface tension, is poorly or not completely soluble in the



medium and ideally is dispersed as fine droplets. Hydrophobic solids (such as hydrophobised silicic acid) are also used as defoamers.

Defoamers based on mineral oil, silicone oil or hydrophobic alkoxylates are of great importance. The classical mineral oils, which contain aromatics, are now used less because of ecological and toxicological concerns. However, replacing them with aliphatic oils often leads to less gloss, e.g. with aqueous dispersion paints.

An important subgroup of defoamers are the organo-modified silicones, in particular the polyether -modified polysiloxanes. The modification gives them a higher surface activity and better spreading properties, which is of particular importance in varnishes and printing inks. The best defoamer depends to a great extent on the type of coating and the additives used. Extensive practical tests are therefore essential in order to develop new coating systems. Typical tests are based on stirring, flowing and rolling. In stirring tests, air is entrained by mechanical energy and the increase in volume measured. After the test, a sample can be poured onto an inclined hard surface. Visual evaluation of the resulting film enables one to draw conclusions on the effectiveness of the defoamer. In roller tests, paint is applied to a defined surface with a roller and the defoamer performance judged by comparison with colour cards.

#### Sugar manufacture

Sugar is now mainly obtained form sugar beet and sugar cane. In the future, cleavage of cellulose (straw) or starch (maize) will become more important in the manufacture of sugar and its derivatives (ethanol). In addition to its uses in the food industry, sugar will play an increasingly important role in the production of basic chemicals, e.g. ethanol, acetic acid or lactic acid.

When sugar beet is used as raw material, these plant roots are first washed. Foam can occur in this first stage due to attached soil particles (clay) and leaching of saponins (surface active glycosides) from damaged roots. Suitable defoamers must be added to control this. In the next step the beet is cut up and extracted with water in the so-called diffuser. Here additional defoamers must be added as the saponin concentration is much higher and the foam would otherwise cause considerable problems.

When the process stars from sugar cane, defoamers are not normally needed in the first stages, as the cane contains only a small amount of natural foamers. In extraction, however, wetting agents are often added to ensure good yield. During crystallisation of the sugar, in refining or fermentation to alcohol these can cause foam, which must be reduced by the addition of defoamers.

As a large proportion of the sugar is used in food, auxiliaries used in its production are regulated. There are, for example, regulations by the FDA (21CFR §173.340) and the EU Guidelines (89/101, 95/2). EU countries also have their own national regulations, such as THV (Nov. 1991) in Germany and the French positive list of Feb. 1989.

Typical defoamers for washing sugar beet are mixtures of mineral oil, native oils, EO/PO



block polymers and fatty alcohols. The amounts used decrease in this order. For extraction, most formulations are based on EO/PO block polymers, fatty acids and their esters. The usual standard test methods are used to estimate the effectivity.

### 6. Test methods

There are many ways in which foam may be tested. In general, methods can be considered in terms of the following three aspects:

- test liquid
- foam generation procedure
- foam measurement method

#### The test liquid

Sometimes the test liquid is well defined by the problem to be investigated. For example, it may be a washing liquor or a metalworking fluid. Often, however, we are interested in the general properties of a surfactant. In this case, the usual procedure is to define a standard concentration and water hardness. In order to select suitable conditions, one should have a general idea of the effect of concentration and hardness on the foaming.

For more fundamental work it may be interesting to consider the relationship of the concentration used to the cmc. At high surfactant concentrations the increased viscosity can affect the foaming.

#### Foam generation

Foam generation methods can be classified into static and dynamic. In static methods, foam is generated and then allowed to decay; typically, foam properties are measured as a function of time starting at the end of foam generation. Dynamic methods use continuous foam generation, which eventually results in a steady state where the rates of formation and decay are equal. In dynamic methods both the steady state and the rate of foam build-up can be measured.

#### Static methods

- Pouring (e.g. Ross-Miles)
- Shaking
- Beating (e.g. perforated disc)
- Stirring
- Brushing
- Nucleation of gas bubbles
- Rubbing
- Foam dispenser

#### Dynamic methods

- Air injection
- Circulation with jet or spray head

A further way of classifying foam generation methods is according to the shear. In practice, however, it is difficult to obtain quantitative data on the shear rates involved.

Foam generation may also be classified according to the bubble size distribution obtained.



In many tests the foam generation procedure has been developed as a simulation of practical applications.

#### Measurement of foam characteristics

The most common way of measuring foam is to determine the foam height against time. Both manual and automated methods are used. There are various evaluation procedures to obtain parameters describing foam stability. In many applications, not only the amount of foam, but also its properties are of importance. For characterisation of foams, bubble size distribution, foam density and foam rheology may be used. Often a visual or sensory evaluation of the foam quality is useful, even though it is partly subjective.

**Table 1** gives an overview of the methods described in section 5.

**Table 2** gives brief descriptions of the testmethods mentioned in the text, together withother commonly used ones.

# Table 1Foam test methods typically used for the applications described in section 5

Application area by industry	Test method No* Name	Foam generation	Para mea	meter sured	rs	
High foaming systems			Initial foaming behaviour	Foam volume	Foam stability	Foam quality
Personal care cleansing (liquids)	4 DIN 53902-2 9 In-house Clariant 14 In-house KAO 15 In-house KAO	Pouring Washing hands Bubbling Stirring	+ +	+ + +	+ + +	+ +
Shaving cream	2 DIN EN 13996 14 In-house KAO	Stirring Bubbling	+	+ +	+ +	+
Foam cleaners	1 DIN EN 12728 4 DIN 53902-2 14 In-house KAO	Beating Pouring Bubbling	+	+ + +	+ + +	+
Textile coating	20 In-house Synthomer	Stirring		+	+	+
Flotation	29 In-house BASF	Bubbling			+	+
Fire-fighting foam	13 DIN EN 1568-1-4	Air entrainment				* *
Low foaming systems Detergents	1 DIN EN 12728 2 DIN EN 13996 3 DIN EN 14371	Beating Stirring Circulation		+ + +	+ + +	
Hard surface cleaners	1 DIN EN 12728 3 DIN EN 14371 15 In-house KAO 16 In-house KAO	Beating Circulation Stirring Circulation		+ + + +	+ + + +	
Dishwashing liquids	1 DIN EN 12728 4 DIN 53902-2 6 In-house BASF 7 In-house Sasol 18 IKW-recommendation	Beating Pouring Stirring Stirring/brushing Rubbing, brushing	+ +	+ + + +	+ + +	+ +
Automatic dishwashing	1 DIN EN 12728 2 DIN EN 13996 3 DIN EN 14371 5 In-house BASF	Beating Stirring Circulation Circulation		+ + + +	+ + + +	
Industrial bottle washing	1 DIN EN 12728 3 DIN EN 14371	Beating Circulation		+ +	+ +	

\*) Number as shown in table 2., \*\*) fire-fighting ability

Application area by industry	Test method No* Name	Foam generation	Parameters measured
<b>Non-foaming Systems</b> Paper fibre production	1 DIN EN 12728	Beating	Initial foaming behaviour + Foam volume + Foam stability Foam quality
· · ·	3 DIN EN 14371	Circulation	+ +
Paper manufacturing	3 DIN EN 14371 24 In-house BASF 25 In-house BASF 26 In-house Ciba 27 In-house Ciba 28 In-house Ciba	Circulation Stirring Circulation, stirring Beating, shaking*** Beating, shaking*** Beating, shaking***	+ + + + + +
Textile pre-treatment Textile dyeing Textile printing and finishing	1 DIN EN 12728 3 DIN EN 14371 12 In-house Ciba	Beating Circulation (Deaeration)	+ + + + + +
Metalworking Cooling lubricants	2 DIN EN 13996 3 DIN EN 14371 8 In-house Clariant 10 ASTM D 3519 11 ASTM D 3601 14 In-house KAO 16 In-house KAO 17 In-house KAO 19 In-house Evonik Goldschmidt	Stirring Circulation Circulation Stirring Shaking Bubbling Circulation Shaking Circulation	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Aqueous coatings	3 DIN EN 14371 21 In-house MÜNZING 22 In-house MÜNZING 23 In-house MÜNZING	Circulation Shaking Stirring Rolling/spreading	+ + + + + + + + + + + + + + + + + + +

\*) Number as shown in table 2, \*\*\*) at the production line

#### Table 2 Foam test method (brief description)

Test method	Description	Remarks
1 DIN EN 12728	<b>Perforated disc beating method</b> Determination of foaming power Liquid is placed in a cylinder. Foam is generated by beating with a perforated disc attached to a rod. Foam volume measured after 1, 3 and 5 minutes.	Simple basic test. Parallel measurements possible with variable conditions (e.g. de- foaming soils). Unsatisfactory differentiation with low-foaming surfactants.
2 DIN EN 13996	Turbine stirrer Determination of foaming and defoaming power <b>Method A.</b> Foam is generated by stirring (5 min, 20°C). Then foam and liquid are poured into a cylinder. Upper and lower foam levels measured over 15 minutes. Defoaming power determined with several defoamer concentrations. <b>Method B.</b> Foam is generated by stirring for a defined time (e.g. 10 min.) during which foam formation is	Test with practical orientation. Can be modified for use in a wide range of applications Test with practical orientation.
	measured with a sensor. Afterwards foam decay observed as a function of time (with sensors).	ge vessels.
3 DIN EN 14371	<b>Circulation test</b> Determination of foaming power and degree of foaming by means of a device that circulates liquid (gear pump) and sprays it from a jet. Foam height is measured during ten minutes circulation and for a further ten minutes afterwards.	Test with practical orientation. Also suitable for testing defoamers. Automatic data evaluation.
<b>4</b> DIN 53902-2	<b>Ross-Miles (modified)</b> Determination of foaming power. Liquid flows freely from a cylinder onto a surface of the same solution at 50°C. Foam height is measured after 30 s, 3 min. and 5 min.	Simple basic test. Sample may not contain sediment or turbidity. Original Ross-Miles method: ASTM D1173.
5 In-house BASF	Automatic dishwasher Rate of spray arm rotation is measured: foam acts as a brake. Test is run with soil (e.g. proteins) over a defined temperature range (20-65°C).	Practically orientated test for low-foaming surfactants and formulations. Automatic data evaluation. Test conditions and machine para- meters can be varied. Measuring force on spray arm gives indirect information on foam volume.
6 In-house BASF	Olive oil test Determination of defoaming action of oily soil. A strongly foaming solution of surfactant or dishwashing liquid is stirred. Olive oil is added in small portions until the entire foam has disappeared.	Simple method to test performance of dish- washing liquids.
7 In-house Sasol	<b>Miniplate test</b> Foam generated by stirring / brushing. Determination of foam behaviour in the presence of soil. Modifications of the original method [21] used by a number of companies as in-house methods.	For dishwashing liquids. Similar to the plate test (No. 18), but uses watch glasses instead of plates; this makes it less time-consuming.

Foam Guideline TEGEWA working group "surface active substances"

Test method	Description	Remarks
8 In-house Clariant	<b>Dynamic foam test</b> Surfactant solution is continuously pumped through a spray head. Maximum foam volume measured [22].	Good method for low-foaming surfactants.
9 In-house Clariant	Panel test Hands and forearms are washed using a defined procedure. The following foam characteristics are assessed: initial foaming, spreadability, volume, creaminess, bubble size and ease of rinsing off. Products are always compared pairwise [23].	Test with practical orientation. Reproducibility can be a problem. Time-consuming.
10 ASTM D 3519	<b>Blender test</b> Foam is generated by shearing for 30s with a kitchen blender. Foam volume is measured.	Test for foam behaviour under high shear.
11 ASTM D 3601	<b>Bottle test</b> Foam is generated by shaking in a closed vessel. Foam volume is measured.	Test for foam behaviour under low shear.
12 In-house Ciba	<b>Deaeration Test</b> Winding spool with raw cotton yarn is placed in a cylinder with surfactant solution. Liquid level falls as air is displaced from the winding spool.	Test for deaeraters. Good performance indicated by rapid initial decrease of liquid level and low final level.
<b>13</b> DIN EN 1568- 1-4	<b>Test for fire-fighting foams</b> Foam generated with fire-fighting equipment (foam pipe) Foamer requirements to produce: 1 - Medium foam for non-polar liquids 2 - Light foam for non-polar liquids 3 - Heavy foam for non-polar liquids 4 - Heavy foam for polar liquids	Foamer requirements and test methods described in the norm.
14 In-house KAO	<b>Bubbling method</b> Air is pumped into the surfactant solution. Foam over- flows into a calibrated cylinder. Foam height and densi- ty, initial foaming rate and density are measured.	Good for rinse-off products (personal care), in particular to evaluate foam quality and stability. Reproducible results.
15 In-house KAO	<b>Reversed stirring method</b> Stir the solution in both directions. Measurement after 30 s, 1min., 3 min. and 5 min.	Good method for rinse-off products (personal care). Measurement of foam quality and stability. Sebum can be used as soil. Position of stirrer in the solution is critical.
16 In-house KAO	<b>Circulation test</b> Circulation until a specified foam height is reached. Measurement after 15 min.	Good method for low-foaming systems, I & I -cleaners, metalworking. All equipment must be carefully cleaned.
17 In-house KAO	<b>Shaking test</b> 30 s shaking, foam volume measured.	Fast screening test für foaming power and foam stability. Foam generation procedure difficult to standardise.

Foam Guideline TEGEWA working group "surface active substances"

Test method	Description	Remarks
18 IKW-recom- mendation	<b>Plate test</b> Foam generated by rubbing and brushing hard surfaces in the detergent solution. Determination of foam behaviour in the presence of soil [24].	Suitable for dishwashing liquids. Determination of foam stability in the presence of fat.
19 In-house Evonik Goldschmidt	Modified circulation test (also known as "Jean Maire"or "Renault Small Station" test) Modified circulation test (3), long circulation times up to 16 h, measurement of foam height and oil sepa- ration at specified times. Variation of water hardness.	Foaming of metalworking fluids.
<b>20</b> In-house Synthomer	<b>Foaming up test with evaluation of foam stability.</b> Foam generation with kitchen blender or planetary stirrer. Measurement of foam density. Evaluation of foam stability according to pre-defined criteria.	Fast and practically orientated method.
<b>21</b> In-house MÜNZING	Shaking test for defoamers in paints and coatings. Foam generation with "Red-Devil-Mixer". Measurement of density and calculation of air content.	Suitable for medium viscosity systems. Mixer ensures intensive, reproducible agitation (air entrainment).
<b>22</b> In-house MÜNZING	<b>Dissolver test</b> Foam generation via intensive mixing with a disc stirrer (dissolver disc, toothed disc). Measurement of foam volume and stability.	Suitable for low viscosity coatings, in which foam in the body of the liquid immediately floats to the surface.
<b>23</b> In-house MÜNZING	Film defoaming Application of the paint to a plastic surface using roller covered with coarse foamed material. This entrains air into the coating film. Visual evaluation of the wet macrofoam and the remaining microfoam after drying.	To test defoaming /deaeration of a coating film.
24 In-house BASF	Determination of the foam value of paper pulp Stir a suspension of wood pulp and additives in a foam channel. Measurement of the area covered with foam.	Testing defoaming /deaeration systems.
25 In-house BASF	<b>Determination of the air content of paper pulp</b> Pumping and stirring a suspension of wood pulp and additives in a circulation apparatus (propeller stirrer). After a defined air content is reached, foam production is stopped and the decrease of the air content over time measured.	Testing defoaming /deaeration systems.
26 In-house Ciba	Determination of air content of paper pulp by ultrasound Increase of the frequency with increasing content of entrapped air.	Testing defoaming /deaeration systems in the paper industry. Instrument: Savcor Sonica Air Content Analyzer, Savcor Group Ltd Oy, Finnland).



Foam Guideline TEGEWA working group "surface active substances"

Test method	Description	Remarks
27 In-house Ciba	Determination of foam volume by measurement of the compression pressure	Testing defoaming /deaeration systems in the paper industry. Determination of entrapped air.
28 In-house Ciba	Determination of entrapped air via density measu- rement with a pycnometer	Testing defoaming /deaeration systems
29 In-house BASF	Flotation cell Direct simulation of the flotation process Measurement of the performance of additives via pro- cess parameters and yield.	Testing flotation auxiliaries (foamers, collectors).

#### Additional foam test methods:

30 ASTM D 1173	Standard test method for foaming properties of surface active agents [original Ross-Miles method]
31 ASTM D 4009	Standard guide for foam stability of hand dishwashing detergents
32 ISO 9120	Petroleum and related products – Determination of air – release properties of Steam turbine and other oils – Impinger method
<b>33</b> BS 5117-1-4	Testing corrosion inhibiting, engine coolant concentrate ('antifreeze'). Methods of test for determination of physical and chemical properties. Determination of foaming characteristics
34 ASTM D 1881	Standard test method for foaming tendencies of engine coolants in glassware
<b>35</b> ASTM D 4921	Standard test method for foaming tendencies of engine coolants at room temperature
<b>36</b> EN 12704	Aqueous adhesives
37 EN ISO 9665	Adhesives – Animal glues – Methods of sampling and testing

#### Contacts for the in-house methods

BASF: wolfgang.spiegler@basf.com or global.info@basf.com

 $\textbf{Ciba:} rainer\_hans.traber@cibasc.com$ 

Clariant: dennis.miller@clariant.com

Evonik Goldschmidt: brigitte.finger@evonik.com

KAO: hamke.meijer@kaochemicals.de

MÜNZING: p.bissinger@munzing-chemie.com

Sasol: britta.jakobs@de.sasol.com

 ${\small Synthomer: } martin.brendel@synthomer.com \\$ 

Ecogreen Oleochemicals: andreas.schroeter@dhw-ecogreenoleo.de

# 7. Literature

#### Reviews

X. Domingo, L. Fiquet, H. Meijer, Tenside Surf. Det., 29, p. 16 ff. (1992)

R. K. Prud'homme, S. A. Khan (eds.), "Foams: Theory, Measurement and Applications" (Surfactant Science Series, Vol. 57), Dekker (1995)

D. Weaire, S. Hutzler, "The Physics of Foams", Clarendon Press (1999)

R. J. Pugh, Advances in Colloid and Interface Science, 64, p. 67 ff. (1999)

D. Myers, "Surfactant Science and Technology",3rd ed., Ch. 8, Wiley (2006)

#### Literature cited

- M. H. Pahl, D. Franke, Chem. Ing. Techn., 67, p. 300 (1995)
- E. D. Manev, S. V. Sazdanova, A. A. Rao,
   D. T. Wasan, J. Disp. Science and
   Technology, 3, p. 435 ff. (1982)
- C. Stubenrauch, Tenside Surf. Det., 38, p. 350 (2001)
- 4. A. Prins, Chem. Ing. Tech., 64, p. 73 (1992)
- T. Engels, W. v. Rybinski, P. Schmiedel, Progr. Colloid Polym. Sci., 111, p. 117 (1998)
- S. Ross, G. Nishioka, Chemistry and Industry, p. 47 ff. (Jan. 1981)

- 7. I. C. Callaghan, in P.R. Garrett (ed),"Defoaming" (Surfactant Science Series, Vol. 45), Dekker, p. 119 ff. (1993)
- 8. R. H. Ottewill, D. L. Segal, R. C. Watkins, Chemistry and Industry, p. 57 ff. (Jan. 1981)
- M. J. Schick, I. R. Schmolka, in M. J. Schick (ed) "Nonionic Surfactants", Surfactant Science Series Vol. 23, Dekker (1987)
- R. Chaisalee, S. Soontravanich, N. Yanumet, J. F. Scamehorn, J. Surf. Det., 6, p. 345 (2003)
- B. Jakobs, B. Breitzke, M. Stolz,
   R. Verzellino: SÖFW Journal, 131, p. 63 (2005)
- S. Ross, Rensselaer Polytech. Inst. Eng. Sci., Ser. 63, p. 1 ff. (1950)
- J. V. Robinson, L. W. W. Woods, J. Soc. Chem. Ind., London, 67, p. 361 (1948)
- 14. G. Nishioka, S. Ross, in Emulsions, inP. Becher and M. Yudenfreund (eds.),"Emulsions, Latices and Dispersions",p. 237, Dekker (1978)
- P. R. Garrett (ed), "Defoaming", Surfactant Science Ser., Vol. 45, Kap. 1, p. 1 ff., Dekker (1993)
- E. D. Goddard, B. Kanner, R. D. Kulkarni Ind., Eng. Chem. Fundam., Vol. 16, p. 472 (1977)
- 17. S. Ross, Colloids and Surfaces A, 118, p. 187 (1996)



- R. Brummer, "Rheology Essentials of Cosmetic and Food Emulsions", 1st Ed., Springer-Verlag Berlin Heidelberg, p. 169 (2006)
- Melliand Textilbericht 76/3, p. 165 ff. (1995)
- 20. J. P. Byers, Manuf. Eng. Mater. Processes, 41, p. 191 ff. (1994)
- 21. R. M. Anstett, E. J. Schuck, J. Amer. Oil. Chem. Soc., 43, p. 576 ff. (1966)
- 22. A. Schrem, D. Miller, W. Skrypzak, 6th Word Surfactant Congress, Berlin (2004)
- 23. a) D. Miller, T. Henning, SÖFW Journal, 130, p. 24 (2004)
  - b) T. Gassenmeier, P. Busch, H. Hensen, Henkel-Referate, 35, p. 84 ff. (1999)
- 24. Ch. Nitsch, G. Hüttmann, SÖFW Journal, 128, p. 23 ff. (2002)

# 8. Glossary

#### Cloud point, cloud temperature

The temperature above which aqueous solutions of certain nonionic surface active agents become heterogeneous by the separation into two liquid phases (coacervation).

#### Defoamer

Substance that prevents foam formation or considerably reduces foam stability.

#### Foam

A mass of cells separated by thin films of liquid and formed by the juxtapostion of bubbles, giving a dispersion in which a large proportion of gas by volume is dispersed in a liquid.

#### Foam booster

A product which increases foaming power.

#### Foam density

Weight of foam divided by its volume (g/L).

#### Foam stabiliser

A product which increases the stability of a foam.

#### Foaming agent, foamer

A substance which, when introduced in a liquid, confers on it an ability to form a foam.

#### Foaming number

Ratio of foam volume to the volume of solution from which the foam was produced.



#### Foaming power

The effectiveness of a product for producing a foam.

#### Initial foaming rate

Quantitative measure of the ability to foam in a short time, e.g. rate of increase of foam volume.

#### Interfacial tension

The tension at the interface between two phases.

#### Spreading ability

The property of a liquid, particularly of a solution of surface active agents, which enables a drop of this liquid to cover spontaneously another liquid or solid surface.

#### Surface active agent

A chemical compound possessing surface activity which, dissolved in a liquid in particular in water, lowers the surface tension or interfacial tension, by preferred adsorption at the liquid/vapour surface or other interfaces.

#### Surface activity / interfacial activity

The action of a substance that modifies the physical properties of a surface or an interface and reduces its surface tension or interfacial tension.

#### Surface tension

The tension acting in the surface of a phase, directed towards the interior of the phase, caused by intermolecular attractions between the molecules at the surface and those located below the surface. The surface tension is expressed in mN/m. Surface tension is a special case of interfacial tension in which the phases are liquid and gas. We are grateful to all those who have provided material for this brochure and for the numerous helpful comments. In particular we thank:

Martin Brendel, Synthomer GmbH, Frankfurt,

Dr. Michael Brock, Sasol Germany GmbH, Marl,

Brigitte Finger, Evonik Goldschmidt GmbH, Essen,

Dr. Christoph Hamers, BASF AG, Ludwigshafen,

Dr. Eberhard Knofe, DHW Deutsche Hydrierwerke Rodleben GmbH,

Prof. Dr. Heinz Rehage, Universität Dortmund,

Dr. Alfred Ruland, BASF AG, Ludwigshafen,

Dr. Heribert Schmitz, MÜNZING CHEMIE GmbH, Heilbronn,

Sandra-C. Schnapper, Verband TEGEWA e.V., Frankfurt,

Dr. Hans Schulze. LANXESS Deutschland GmbH, Leverkusen,

Prof. Dr. Ing. Lothar Schulze, SITA Messtechnik GmbH, Dresden,

Ute Timpe, v-com, Ingelheim

Dr. Claudia Wood, BASF AG, Ludwigshafen.



