TEGEWA

The busy compounds

A short introduction to the world of surfactants

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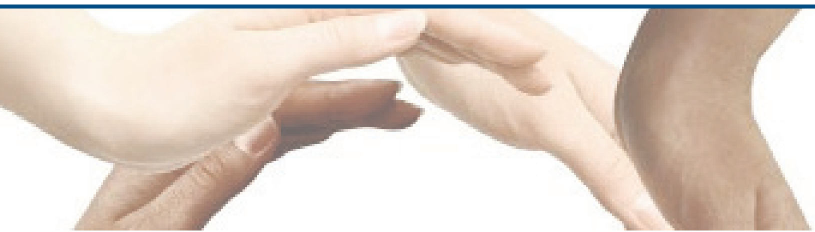

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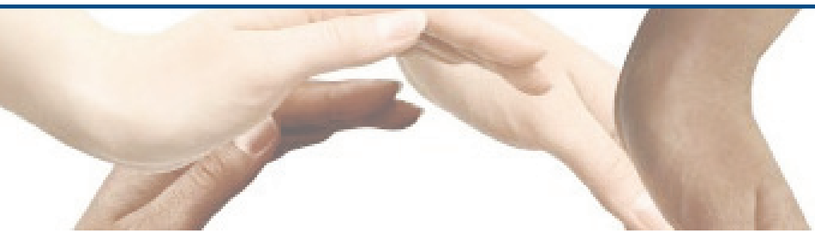
Some introductory remarks

Natural and synthetic surface or washing active substances (surfactants) are so important in everyday life that we are generally not aware of all the things that we owe to them. Just imagine a day without surfactants. Toothpaste would not be a homogeneous paste – it would not foam while cleaning your teeth or disperse properly. There would be no shaving foam at all. Not only would face cream look unappetising, the skin would hardly be able to absorb it. The PVC floor in the office would be as smooth as glass and the printer would have a maximum resolution of one centimetre. The dishes from last night's meal would not be properly cleaned, not to mention the laundry. There would be no such thing as a relaxing foam bath. And without natural surfactants in your digestive juices, your evening meal would lie so heavily in your stomach that you would not be able to fall asleep. These are just a few of the many examples that show how essential the job is that surfactants do both in industrial processes and in your personal life. Furthermore, there are already indications that special surfactants may be used in the future to increase the yield of oil deposits or that completely novel detergents and solvents or even plasticisers may be developed based on nanotechnology. Or did you think that surfactants could only be found in washing powders?

The purpose of the present brochure is to provide factual information about the chemistry of surfactants and their range of applications. When the first printed edition of this informative brochure was being written in the middle of the mid-1980s, environmental awareness was on the rise in society, politics and industry. At the time, surfactants became the focus of public interest, because they are one of the most widely distributed groups of chemical substances in daily demand – both in households and in industrial applications. They are also significant in terms of volume: more than two million tonnes of surfactants are now being used in Western Europe alone each year. Considerable amounts end up in wastewater at the end of the usage life cycle. Science, too, has worked extensively with surfactants over the years and the above factors have led to a great number of studies being available on the market, for example as regards their biological degradability.

The TEGEWA Association and the section of the German chemical industry that it represents responded to the public's critical interest by publishing a brochure in German entitled "The busy compounds, what is worth knowing about surfactants" ("Die fleißigen Verbindungen, Wissenswertes über Tenside"). Its success exceeded all expectations. More than 150,000 copies were distributed to interested parties in Germany. Schools were especially interested and used it as a valuable supplement for their chemistry lessons.

This new edition, which is now also available in English, will not only include the history of the origin of surfactants, their fields of application and comprehensive information about surfactant chemistry, but also current findings and new developments. The use of technical terms is unavoidable at times, and therefore the most important terminology has been explained in a glossary. A few aspects of the chemistry of surfactants will also be touched upon, but in such a way that they can also be understood and appreciated by readers who are not "at home"



with chemistry. The chapters do not necessarily build up on each other; they can be read in a different order or selectively. However, it is advisable to take a little time and read the brochure through from the first to the last page, for example while travelling on a train or airplane to a business associate. Having reached the end, the new staff member in the surfactants business division, the editor planning to write a background report on surfactants or the chemistry teacher who would like to introduce her pupils to an interesting class of substances with a high application potential will have a foundation of basic knowledge of the busy compounds that can later easily be used for further study.

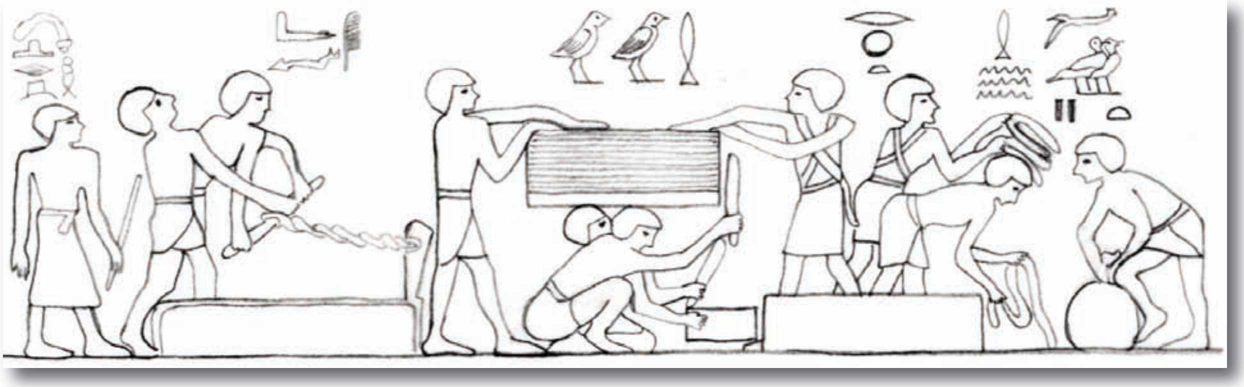
The history of surfactants

Brief historical outline

2500 BC:	"Discovery" of soap by the Sumerians
7th century AD:	The art of soap making reaches Spain
14th and 15th centuries:	Development of the craft of soap making in Europe
Beginning of the 19th century:	Decoding of the structure of soap
Beginning of the 20th century:	Emergence of surfactant chemistry, extensive research and expansion of its fields of application

Soap was the first surfactant that was artificially made by humans from fat and alkali (the term comes from the Arabic for "potash" or "ashes"). A soap recipe scratched on a tablet of argillaceous slate dating from about 2500 BC provides evidence that the Sumerians were already producing soap from wood ash and animal or vegetable fat in Mesopotamia.

In antiquity, soap was known to be an efficient medication; however, it was also used as a "hair-setting lotion". The Gaols and Germanic



Laundry in Egypt (as shown in a wall painting from about 600 BC)

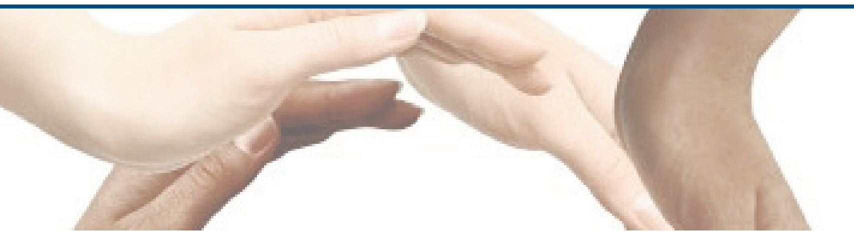
people used soap for bleaching and fashioning their hair and discovered, when later rinsing it with water, that foam developed that promoted the cleaning process. The dark-haired Roman women procured spheres of soap from the Germanic border provinces and rubbed it into their hair. They found that their hair turned blond after it had been exposed to the sun for hours. It was then only a small step from washing the hair to cleaning the entire body and clothes. As early as in the 2nd century BC, Galenus, a physician living in Rome, was recommending soap for use not only as a medicinal substance, but also as a cleaning agent.

The Moors brought the art of manufacturing soap to Spain in the 7th century AD. It was there and in the neighbouring south of France that the first European centres of soap making developed. Soap began to evolve as a commodity. Further centres of soap making were established in Venice, Genoa, Vienna, Augsburg and Nuremberg. The French and Italian Mediterranean ports were the first major trading centres for soap. Curd soap is still known as "Savon de Marseille" in France today.

The 14th and 15th centuries saw the development of soap works. They maintained a leading role in the manufacture of soap up to the start of the industrial era. The advances made in chemistry and the development of industrial production methods made it possible for synthetic surfactants to become one of the most important groups of substances in auxiliary and detergent chemistry.

From 1811 to 1823, the French chemist Michel Eugene Chevreul succeeded in decoding the structure of soap, the most basic surfactant. As a result, it was possible to establish a connection between soap's molecular structure and its cleaning effect and to synthesise further substances with similar surfactant properties.

Since the properties of classic soap, such as its alkalinity (= basic characters, as for example the danger of skin burns), its sensitivity to hard water, its insolubility in acids, its instability to other chemicals and its poor skin compatibility, left much to be desired, extensive research was carried out to find better solutions in the late 19th and early 20th centuries. German research scientists were key in providing the impetus for the rapid development of surfactant chemistry. The economic significance of surfactants grew concurrently with their uses. The number of patents jumped sharply from 1930. Substantial investments were made in newly emerging markets. All leading chemical companies in almost all industrial nations were



involved in a dynamic race for the development of ever better surfactants.

Today, surfactant chemistry is one of the best researched and scientifically developed fields. Very substantial contributions were made by the evolution of new methods in the analysis and structural decoding of surfactant molecules, the various chromatographical methods, infrared and ultraviolet spectroscopy, the measurement of light scattering and nuclear magnetic resonance as well as examinations with X-rays, isotopes and electron microscopes.

Surfactants – irreplaceable in nature as well

The term “surfactant” is a blend of surface active agent. It lowers surface (interfacial) tension. What is meant here is the force that holds two phases, such as a liquid and a solid that are in contact with each other, together and leads to tensions at the interfaces between the phases.

Surfactants are in fact absolutely vital: flora and fauna (including humans) need to produce surfactants to live and survive. In the organisms of plants, animals and humans, liquids and solids have to overcome numerous barriers – from the digestive tract to the blood, from the breathing air through the lung to the blood and vice versa, from cell to cell – in order to give and sustain life. Lecithin and its related substances are examples of such natural surfactants: as constituents of the outer and inner cell membranes, they prevent unwanted substances from penetrating the cells. In other cases, they pave the way to the interior of the cell.

Thus natural surfactants play an important role in metabolism. Without natural surfactants, our bodies would not be able to cope with such an important function as breathing. They facilitate the exchange of gases via the lungs into the blood and vice versa and ensure that the pulmonary alveoli – those parts of the lungs in which the gas exchange between the inhaled air and the blood takes place – do not stick, but reopen for the next breath. Finally, fat could hardly be digested without surfactants: The natural surfactants that are produced most diligently are the bile acids originating in the liver, which incidentally people also use as gall soap. It is their job to prepare the fats from food for digestion.

Human livers are no less productive than the chemical industry. Each year, just under 82 million people naturally produce approximately the same amount of surfactants in their livers as industry manufactures synthetically for use in Germany: more than 500,000 tonnes.

The chemistry of surfactants

Structure

The molecular structure of all surfactants, including soap, has its own peculiarity. In simple terms, imagine a surfactant molecule as a small rod with a thick end like a match. This “head” is water-loving (hydrophilic), whereas the tail is water-repellent (hydrophobic) and turns away from water. The opposing features of the two components of the surfactant molecule explain its surface-active properties: the tail is rejected by water, the head attracted by it.

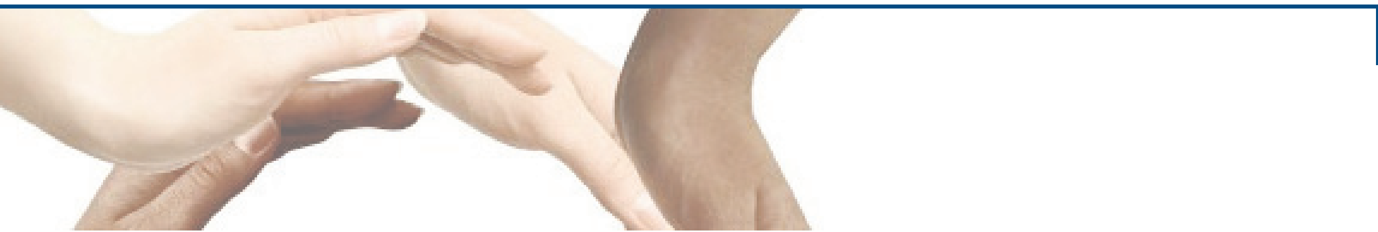
Graph of the match model:

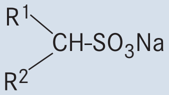
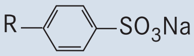
Hydrophobic component, i.e. water-insoluble or fat-soluble

Hydrophilic component, i.e. water-soluble or fat-insoluble

The hydrophobic end is similar in all surfactants and consists of a long-chain non-ionic hydrocarbon rest, sometimes in connection with a benzene ring. The hydrophilic end can vary greatly but normally bears an electric charge. This is why surfactants are divided into four classes depending on the character of their hydrophilic group: anionic, non-ionic, cationic and amphoteric (= zwitterionic) surfactants. The non-ionic (= “non-polar”) hydrocarbon rest can be varied arbitrarily, just like the hydrophilic group. This results in an almost endless variety of possible structures. The following table shows some important representatives of common surfactants and lists examples of the areas of application for the specific surfactants or for combinations of surfactants (surfactant mixtures).

Surfactant class	**Examples**	**Variants** (hydrocarbon rest)	**Chemical name**	**Use**	**Abbreviation**
 Anionic surfactant	$R\text{-}CH_2COONa$	$R = C_{10} - C_{16}$	Alkyl carboxylates	Body care; household cleaning	Soap
	$R\text{-}CH_2\text{-}O\text{-}SO_3$	$R = C_{11-13}$	Fatty alcohol sulphates	Cosmetics	FAS
	$R\text{-}CH_2\text{-}O(\text{-}CH_2\text{-}CH_2\text{-}O)\ n\text{-}SO_3Na$	$R = C_{11-13}$ $n = 2$	Fatty alcohol ether sulphates	Cosmetics; household cleaning	FAES

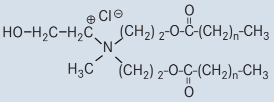


Surfactant class	**Examples**	**Variants** (hydrocarbon rest)	**Chemical name**	**Use**	**Abbreviation**
Anionic surfactant		$R^1+R^2 = C_{12} - C_{16}$	Secondary alkane sulphonate	Liquid detergents; dishwashing detergents	SAS
		$R = C_{10} - C_{13}$	Linear alkyl benzene sulphonate	Detergents	LAS

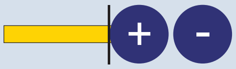
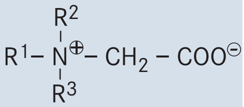
Anionic surfactants are washing-active substances that have a negatively charged hydrophilic functional group. Together with the non-ionic surfactants, they are the most important class of surfactants today. Besides the classic soaps, they include fatty alcohol sulphates and fatty alcohol ether sulphates as well as alkyl benzene sulphonates, which are one of the most important detergent surfactants on account of their favourable technical properties.

 Non-ionic surfactant	$R\text{-}CH_2\text{-}O(\text{-}CH_2\text{-}CH_2\text{-}O)nH$	$R = C_{10-18}$, $n = 3-15$	Fatty alcohol ethoxylate	Detergents and cleaning agents; emulsifiers	FAEO

The hydrophilic end of the **non-ionic surfactant** consists of strongly polar chemical bonds (-OH = alcohol; –O– = ether), and the hydrophobic end consists of a long-chain hydrocarbon rest, similar to other surfactant groups. Non-ionic surfactants include ethoxylated fatty alcohols or fatty acids as well as alkyl polyglucosides (sugar-based surfactants). In the case of most non-ionic surfactants, solubility decreases as the temperature rises. The surfactant and aqueous phase separate from a critical temperature – the cloud point. Anionic and non-anionic surfactants are combined in most modern detergents and cleaning agents; the advantages of the individual surfactants can supplement each other optimally.

 Cationic surfactant		$n = 10 - 16$	Quaternary dialkyl ammonium ester	Fabric softeners	Ester quats

In **cationic** surfactants, the hydrophobic hydrocarbon rest is bonded to a hydrophilic, nitrogen-containing group that has a positive charge (R_4N^+). Cationic surfactants are for example used as softeners for textiles. Certain cationics have a biocidal effect and are therefore used as disinfectants. In hair rinses, they prevent the hair from becoming statically charged, make it easier to comb and protect it from mechanical damage (e.g. brushing).

Surfactant class	**Examples**	**Variants**	**Chemical name**	**Use**	**Abbre-viation**
 Amphoteric surfactant (ampho-surfactant)	 $R^1-\overset{R^2}{\underset{R^3}{N^{\oplus}}}-CH_2-COO^{\ominus}$	$R^1 = C_{12-18}$, $R^2, R^3 = CH_3$	Betaine	Cosmetics; detergents	

Amphoteric surfactants contain a negatively and positively charged group at the hydrophilic end of the molecule. Betaines are the most important synthetic representatives. There are also important natural amphoteric surfactants, e.g. the lecithin of egg yolk. These surfactants are used in combination with anionic surfactants in hair shampoos and other cosmetic products since they greatly help to improve the skin compatibility of anionic surfactants and to stabilise foam.

Modes of action

Lowering surface tension

The surface tension of water is what enables small insects to walk on its surface or a razor blade or paper clip to float on it. This means that the surface of a liquid behaves like an elastic film and works to maintain as smooth a state as possible with minimal three-dimensional extension.

The angled structure of the water molecule means that it has two polar ends (Fig. a). Individual water molecules bond to each other with opposite polarisation (Fig. b) and are held together by the resulting electrostatic interactions. This kind of cohesion is known as a hydrogen bridge (bond).

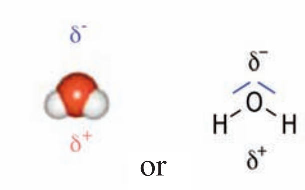


Fig. a

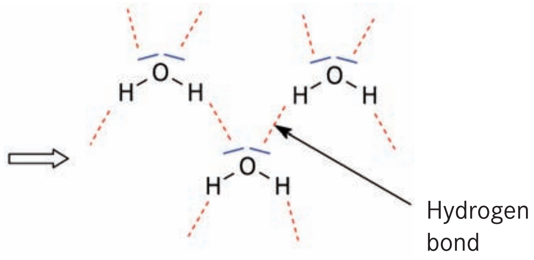
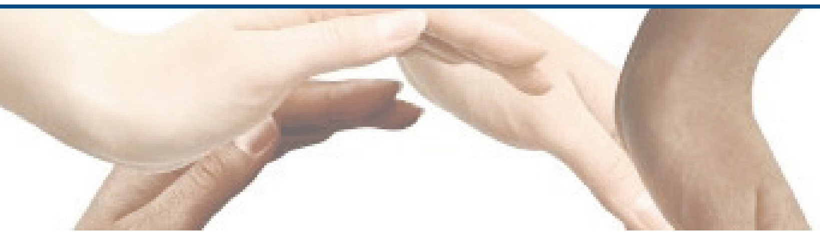
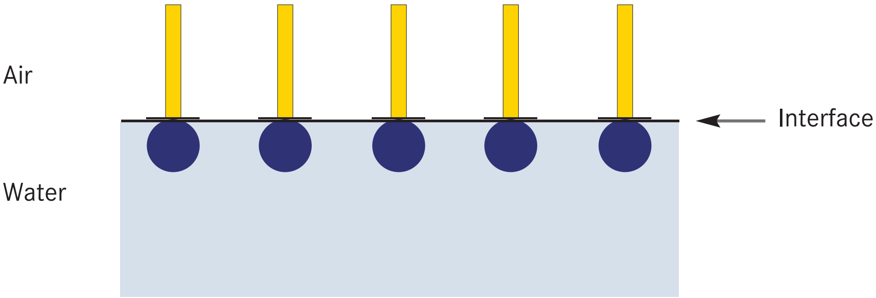


Fig. b



The extent of the surface tension depends mainly on how strongly the liquid molecules are attracted to each other, in other words the strength of the hydrogen bridge. Water has a very high surface tension on account of the high polarity of the water molecules and the resulting strong hydrogen bridges.

Surfactant molecules considerably lower this surface tension. This can be explained by their surface activity, from which the name **surf**ace **act**ive **a**ge**nt** was derived. Interfaces are the contact areas between systems (phases) of different aggregate states (e.g. water-air interface). However, an interface is also possible between two liquid phases that do not mix – as for example oil and water.

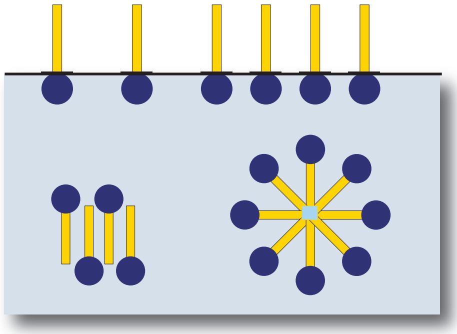


The addition of surfactants weakens the cohesion of the water molecules and thus reduces the surface tension: each non-polar end of a surfactant molecule endeavours to enter a non-polar environment (= air) and the hydrophilic end of the molecule projects in the direction of a polar aqueous solution. This positioning to phase interfaces is advantageous for surfactants in terms of energy because the hydrophobic and hydrophilic ends of the surfactant molecule can arrange themselves there in such a way that molecular rejection forces are minimised with the particular phase and molecular powers of attraction are maximised. Polar groups of the surfactant can now be found between the water molecules on the surface of the water. This reduces the attraction between the water molecules resulting from the strong hydrogen bridge and weakens the cohesion of the water molecules.

If a few drops of a washing-up liquid were thus added to the water, the insect, the razor blade or the paper clip would immediately sink – there would no longer be a “film” on the water.

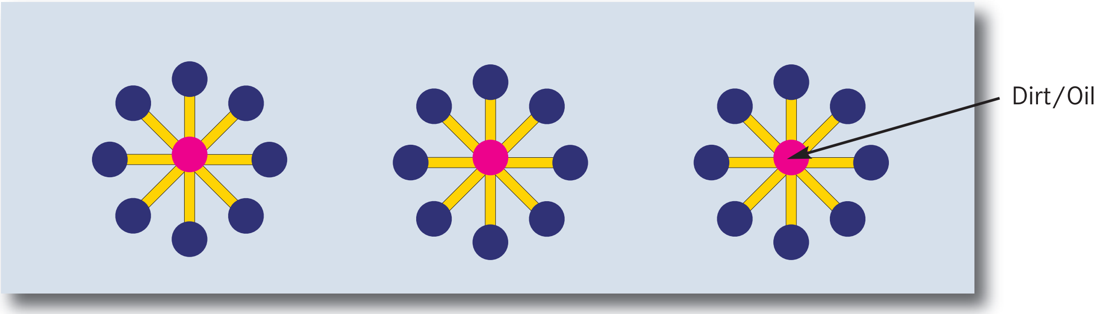
Formation of “micelles”

When the phase interfaces are completely occupied by surfactant molecules, the surfactant molecules diffuse into the solution and clump together there in the form of spheres. Such spheres of surfactant molecules are called micelles (Latin: mica = grains). These are particle clusters of 50 – 1000 molecules in various shapes depending on the particular surfactant.

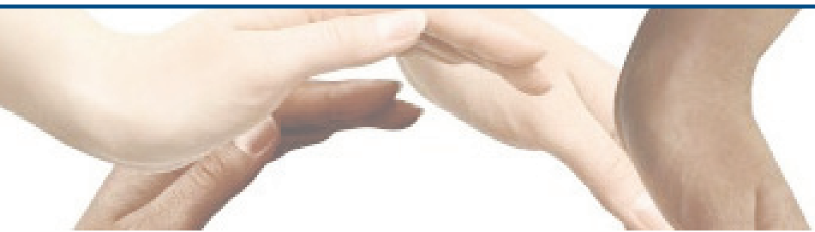


In micelles, the hydrophobic hydrocarbon chains point towards the interior of the spheres, while the hydrophilic groups form hydrocarbon bridge bonds with water molecules. For each surfactant, there is a specific concentration above which micelles begin to form. It is known as the critical micelle concentration (CMC). Since micelle formation starts precisely at the surfactant concentration at which the surface is substantially occupied, there is no further change in the surface tension of the liquid when more surfactant is added. Many properties of surfactant solutions, such as foaming, washing effect and emulsifying power, will not unfold their full effect until the critical micelle concentration has been reached.

The CMC value depends greatly on the structure of the surfactant. Ionic surfactant molecules mutually repel each other on account of their charge. In this case, micelles are only formed at a fairly high concentration. Non-ionic surfactants do not have a charge with the result that the concentration required for micelle formation is considerably lower. For their practical application, this means that lower amounts of non-ionic surfactants are required in order to achieve the full effect of the surfactant. The shape of micelles is also influenced by the surfactant concentration. Diluted surfactant solutions mainly contain spherical micelles whereas bigger rod-shaped micelles can be found at higher surfactant concentrations.



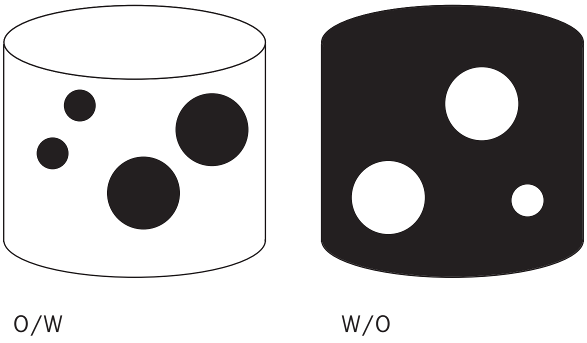
Hydrophobic substances (e.g. oils) can be taken up into the interior of such spherical micelles and then dissolved in water (= solubilised). This explains the emulsifying effect of surfactants; it will be described in more detail in the following section.



Emulsifying power – dispersing power

According to the label on the jar, mayonnaise contains oil and water. If you want to make some mayonnaise yourself and you pour oil into a glass bowl and then add water, you will find that the two liquids do not mix with each other: the heavy water remains at the bottom and the lighter oil floats on top. The two liquids cannot be mixed even if a whisk is used. Although some drops of water move up to the oil and some drops of oil move down to the water, the oil returns to the oil and the water to the water as soon as you stop stirring: the phases separate again. The trick to making homemade mayonnaise is to add egg yolk. This contains natural, surface-active substances – for example lecithin – that make mixing, i.e. “**emulsifying**”, possible. Emulsifiers have an affinity for both liquids. The lecithin in egg yolk lowers the interfacial tension and mayonnaise can then be made by stirring. Its oil concentration may be as high as 65 per cent.

If very small drops of oil, e.g. mineral oil, are surrounded by water, we call this an “oil-in-water” (O/W) emulsion. However, if water is finely dispersed in a non-aqueous liquid, a “water-in-oil” (W/O) emulsion is formed.



Many examples of emulsifiers can be found in food: cow’s milk is an O/W emulsion, in which approximately 3.8% of fat is dispersed in the aqueous phase. Butter, however, is a W/O emulsion, in which up to 20% of water may be dispersed.

In the best known and most widely used application of surfactants – in washing and cleaning – not only liquid oils but also solid residues, such as dirt particles, are removed from fibres and surfaces and held in solution. This process is known as “**dispersing**”. The surfactant ensures that the solids remain in solution and do not settle again. But not only that: the surfactant molecules also fragment and enclose the dirt particles. In this way, the dirt is removed with the suds.

Wetting water-rejecting (hydrophobic) surfaces

Many surfactant applications are based on the fact that they enable or improve the wetting of the surface of a solid object with a liquid. The degree of wetting depends on the liquid’s surface tension and the structure of the solid. Wetting is facilitated when the liquid has low surface tension and the solid has high surface tension. Since glass for example has a significantly higher surface tension than many plastics, glass is wetted by water whereas hydrophobic surfaces such as polyester or polyamide are not.

Surfactants that are used to wet surfaces more effectively are known as wetting agents. Washing the laundry is doubtlessly the best known example for the use of the wetting properties of surfactants. For an effective washing process, a textile fabric needs to be wetted as thoroughly as possible to remove not only the stain on the surface, but also the dirt deeper in the fabric. Further examples in which surfactants are used as wetting agents are cosme-

tics, painting, pharmaceutics and crop protection – further details can be found in the chapter on “Fields of application of surfactants”.

Foaming

Finely pored foam is formed when small pieces of horse chestnuts are mixed with water. Stirring a little water into a mixture of egg yolk also creates foam. Furthermore, it is common knowledge that foam is formed by adding washing-up liquid to water.

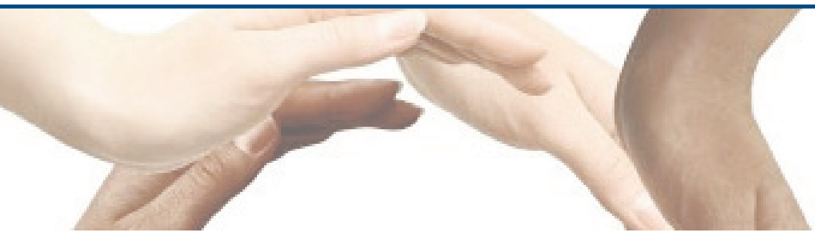
Horse chestnut, egg yolk and washing-up liquid have something in common: they contain natural or synthetic surfactants. They lead to the formation of foam, thus encouraging the fine dispersion of air in water.

The ability of surfactants to form foam is used for a great variety of applications. For example, a number of cleaning agents are available as foams, such as oven sprays. On account of its large surface, foam has a strongly adsorbing effect and can take up many dirt particles. Thus wool detergents are designed to foam vigorously so that cleaning is effective with a lesser mechanical impact in the washing machine, which prevents felting. Greater mechanical wear (friction) would otherwise be expected.

In the case of cosmetics, ecological and economic factors are important, but these are superseded by dermatological properties – such as mildness and skin compatibility. Foamability is also important. Surfactant residues on cleaned hair and skin surfaces are symptomatic of overdosing, which is avoidable. The formation of foam in a foam bath is desirable because it promotes relaxation.

Although the foam formed by washing-up liquids does not actually clean, it is an important indicator for the dirt-holding capacity of the rinsing water (liquor). If the foam layer on the rinsing liquor continually collapses, this generally indicates that its cleaning power has been exhausted.

Soap bubbles can easily be made with a mixture of water, glycerol and washing-up liquid. The brevity of their existence is explained by the fact that the water molecules between the layers of surfactants flow downwards, and as the polar groups of the surfactant molecules come into contact with each other in the upper area of the soap bubble, they repel each other, bursting the soap bubble.



Foam formation is sometimes undesirable. Dishwasher detergents must not foam too much since this would reduce the mechanical cleaning effect of the spray jets. Nor is excessive foaming desirable in a washing machine; the foam should not pour out of the washing machine. Similar considerations apply to washing lines in the beverage industry. In these areas, various soaps, silicon oils or paraffin oils are effectively used as anti-foaming agents (defoamers).

Therefore, the tendency of surfactants to form micelles enables their wide range of possible applications as wetting agents, emulsifiers, dispersing agents and foaming agents. By combining various surfactants and additives, surfactant research has succeeded in achieving the desired effect for a particular application. However, the search for new combinations and fields of application is ongoing since new problems that require new solutions continue to emerge, even for known applications, or because new fields of application have been found for surfactants that no one had imagined a few years back.

The economic significance of surfactants

Surfactants are used for a wide range of applications. In Western Europe, they are one of the few chemical compounds that are used in a total amount of considerably more than 2 million tonnes each year. Apart from the reasonably priced standard surfactants for classic fields of application, there are also many special varieties with significantly higher value added.

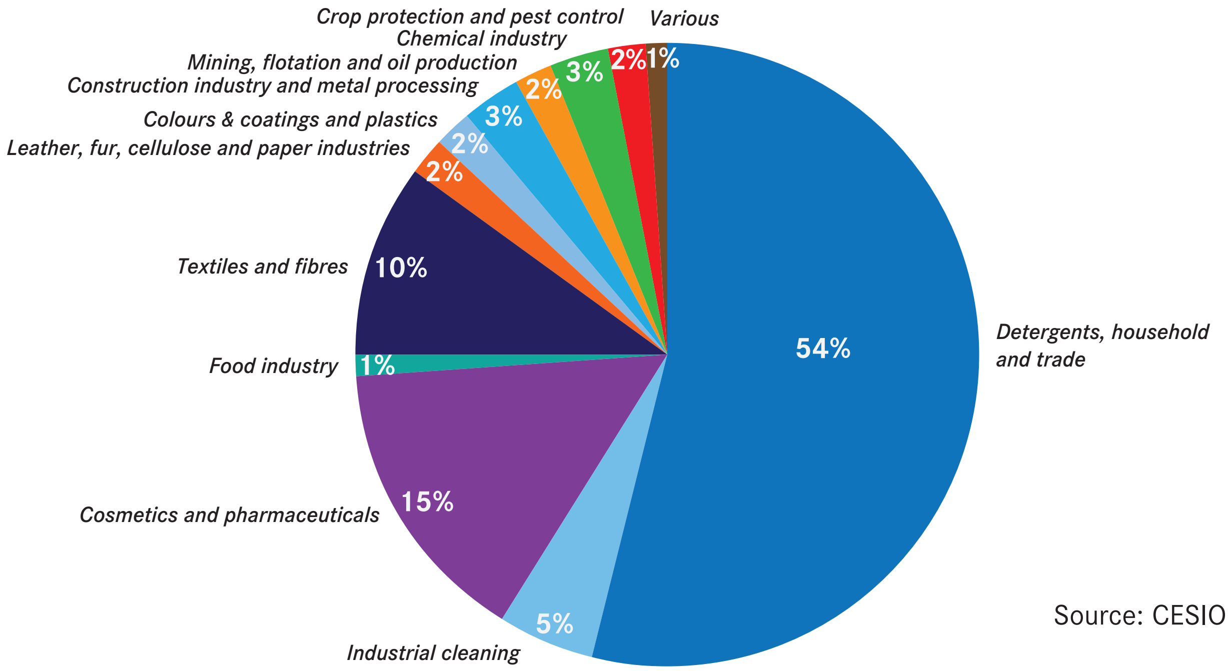
A few of the most important kinds of surfactants are fatty alcohol ethoxylates, LAS and alcohol ether sulphates. These three groups of surfactants account for more than three-quarters of the total West European production output.

By far the largest proportion of common surfactants are currently being produced and marketed by major international companies. According to a rough estimate, Germany accounts for about 20 per cent of surfactants consumed in Europe, i.e. approximately 500,000 tonnes of the total of approximately 2.5 million tonnes consumed in Western Europe.

However, the economic significance of surfactants is not reflected simply by the scale of their production volume. Since surfactants have important functions in many areas and applications and constitute essential system components in mixtures, they are indispensable and of economic significance for industry and the consumer goods industry to a degree far beyond their substance-specific value. In the following chapter, the various fields of application are presented briefly in an overview.

Fields of application of surfactants

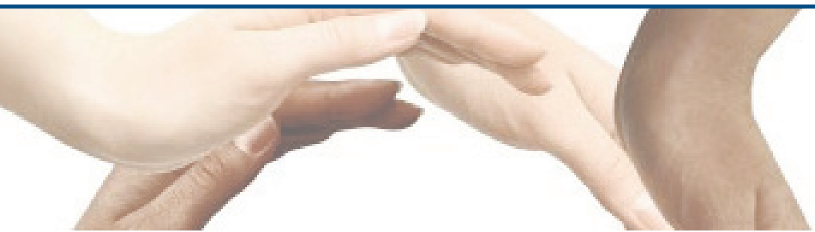
Overview: use of surfactants in Western Europe (share of total consumption in %; shares have remained constant over the last few years)



Source: CESIO

Detergents and cleaning agents

Detergents are not only the best known of the large number of surfactant applications. Detergents for household and trade account for approximately 50% of the total consumption of surfactants in Europe. Surfactants are a decisive element of all modern detergents because they can remove fat and dirt from fibres. In line with the wide variety of stain types, the surfactant fraction of a detergent consists of a balanced combination of various surfactants – as a rule anionic and non-anionic compounds. Together with the other constituents, they have to accomplish more than just clean laundry optically and hygienically. From the moment that the package is opened until the last cup is emptied, the detergent must be and remain free-flowing, be easy to store, not lump, dissolve easily and be capable of being flushed into the washing machine. In order to guarantee all this, the production of detergents requires a great deal of scientific and process engineering skills. The ability to wet also plays an



important role in washing and cleaning processes. Depending on which liquid is involved, which material the surface is made of and what its nature is – for example in terms of roughness – the liquid wets the surface more or less thoroughly.

Surfactants have played a decisive role in making almost all household cleaning jobs easier – with greater hygiene, gloss and better protection of the products to be cleaned. Areas that illustrate how well they can remove fat and dirt are dishwashing by hand and with a machine, cleaning kitchens and bathrooms, maintaining polished floors, cleaning shoes with liquid shoe polish and car care. Furthermore, materials treated with surfactants can be cared for and cleaned more easily, such as carpets. Surfactants prevent these from becoming statically charged, which means that they no longer attract dust particles.

Further examples of applications

Surfactants are now being used in such a wide range of areas that it would be impossible for this brochure to provide a complete overview of them. Instead, it will provide a series of impressions of the enormous overall performance and significance of surfactants. First of all, surfactants are not only washing-active – they wet, displace oil, fats and dirt, foam or defoam, render soluble what is insoluble (solubilise), blend non-miscible liquids (emulsify), can permanently suspend fine particles in a liquid (stabilise suspensions), dissipate materials into fine particles (disperse), attach to surfaces and give these new properties, and do many other things. Such a wide range of properties can be put to numerous uses. Here are a few further examples to illustrate this.

Beverage industry

The high-speed washing of bottles and the disinfection of pipes or tanks would be unthinkable without surfactants. Their wetting action means that cleaning is more effective and labels peel off more easily. No water remains in the cleaned bottles and they shine brightly. All this is carried out without any foam problems in spite of high loads with cleaning rates of more than 100,000 bottles per hour and washing line.

Chemical industry

Surfactants are indispensable, even in those areas where their performance is not immediately obvious to consumers, such as the chemical industry.

Surfactants are beneficial to reactions in heterogeneous systems; for example they act as transport agents in phase-transfer catalysis.

By spraying surfactant solutions onto powdered chemicals, the latter can be processed more effectively and more safely.

The flowability of powdery substances (e.g. fertilisers) is increased by surfactants because they help prevent lumping.

Plastic dispersions contain surfactants to emulsify inputs and improve wetting properties.

Colours, coatings and dispersions

Surfactants act as dispersing agents for colour pigments and carbon black and enable them to be ground with energy savings. They stabilise the colours and simplify restirring and homogenisation. Oil-soluble surfactants also stabilise solvent-containing coatings and modern water-based coatings would not be conceivable without specialised surfactants. They improve the electric conductivity of powder coatings and make the particularly rustproof electrophoretic coating process possible – the electric attraction of the coating particles by electrically charged materials. Today, for example, this process is used to protect car bodywork. As defoamers, they prevent cratering when painting and spray coating. As levelling agents, they increase the evenness and gloss of the coating surface. In painting, the applied paint must wet the canvas to obtain a uniform film of paint – surfactants make this possible as well.

Construction industry

Surfactants are required as plasticisers for fluid concrete. They also act as air-entraining agents in lightweight concrete, as concrete compaction agents and grouting aids. As a mortar additive they assist plastification and act as sealants or stabilisers. They are indispensable for the formulation of shuttering oil emulsions, for the production of foamed gypsum boards and in paint dispersions. Surfactants are also used for processing bitumen in road construction.

Cosmetics

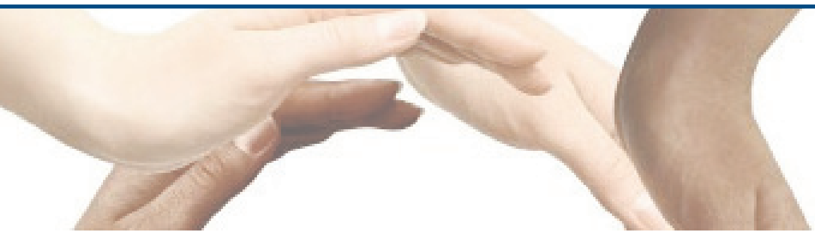
Surfactants are essential constituents of or indispensable agents in almost all cosmetic products and compounds: they clean and foam in shampoos and hair rinses, shower gels, soaps, liquid soaps and bath additives.

Shampoo surfactants that make the eyes sting have long been a thing of the past. Even for adult body and hair care, mild “baby shampoos” with surfactants that are gentle to the skin and sensitive additives have become standard.

Skin-compatible surfactants act as emulsifiers and stabilise the fine water or oil droplets in creams and thin lotions. Emulsions are quickly absorbed by the skin, do not cause a shiny, greasy film or leave any grease spots on clothing – neither in skin care cosmetics nor in sunscreen products. Surfactants also enable the fine dispersion of colour pigments in make-up and lipstick.

They disperse perfumes in toilet waters, aftershaves and hair lotions. Surfactants are just as common in hair dyes and hair care products as in shaving creams and toothpastes.

The spectrum of surfactants for body care and cosmetics is extremely broad and ranges from particularly skin compatible (baby care) or mucous membrane-compatible (toothpastes) to tasteless, strongly or weakly foaming and stable to excessively fatty oils – and all of this in a liquid form, as a paste, powdery, clear, milky, pearlescent, etc.



Crop protection and pest control

Here, too, the emulsifying and dispersing properties of surfactants are particularly appreciated.

When applying crop protection agents, the leaves must first be wetted since the active substances are often taken up through the leaves. Surfactants prevent the spray solution from rolling off the leaf surface, enable uniform dispersion of the active substance on the leaf and make it easier for the active substance to penetrate the leaf through gaps and membranes. Surfactants increase the effect of the agents used.

Crude oil production

As crude oil is extracted, it becomes increasingly diluted during production, leading to the formation of water/oil emulsions. The addition of surfactants (crude oil emulsion breakers) results in the rapid and complete separation of the emulsion into the oil and water phases.

When conventional production techniques are used, significant quantities of crude oil remain in the deposits. The degree of deoiling can be improved by injecting water; this is optimised by washing out with surfactant solutions (enhanced oil recovery). Where the drill-hole is badly bent, oil-based drilling fluids minimise losses through friction and the collapse of surface layers. Surfactants are used to produce the necessary water/oil emulsions. In protracted drilling operations, very fine dust particles accumulate in water-based flushing liquids; when they stick together (agglomerate), viscosity may rise to undesired levels. The addition of surfactants redisperses the solids; the viscosity of the flushing liquid in the drill hole remains constant.

Fire fighting

Surfactant-containing extinguishing foams (e.g. foam carpet at airports) quench fire by stopping the supply of oxygen and make wetting possible. Specific surfactants enable water foam to swim on burning petrol, covering this completely.

Food

Margarine cannot be produced without adding surfactants that are suitable for use in foods and identical to those found in nature since the water and fat phases would immediately separate from each other and no stable emulsion would be formed.

Ice cream would not be smooth and creamy without emulsifiers because large water crystals would form, giving it a very rough consistency.

Mayonnaise can be made without the addition of artificial emulsifiers since the lecithins in the egg yolk are surfactants. However, synthetic emulsifiers have to be added if eggs are not used in industrial production on account of the risk of a salmonella infection.

Bread, cakes and pastries have greatly improved sensory properties (crumb and crust) through surfactant-like emulsifiers and remain fresh for prolonged periods.

Gastronomy

Surfactants are used for dishwashing in pubs, restaurants and canteens. It is primari-

ly due to their wetting and draining behaviour that china and glass come out of the machines clean, shiny and free of stains. In order to clean effectively, modern dishwashers operate at high water pressure. This means that detergents should not produce much foam. There are even special detergents for beer glasses since the surfactants normally used in dishwashers inhibit the formation of foam required for beer.

Household

As already mentioned above, the use of products containing surfactants in private households is one of the most important fields of application. Today, the heavy work is done by washing machines with the assistance of appropriate surfactant combinations. Effective surfactants that do not harm textiles or the hands are available for delicate fabrics. Special surfactants are used as fabric softeners and keep freshly laundered articles of clothing from rubbing against the skin. At the same time, they prevent fibres from becoming electrically charged. They thus ensure that the cleaning effect lasts longer because charged fibres and hairs attract dirt particles. Special low-foaming surfactants do most of the work in the dishwasher, whereas there are also foaming and skin-compatible surfactants for washing up by hand. Surfactants with a high cleaning power that require no subsequent wiping are available for floors, windows and bathrooms.

Leather

Surfactants are involved in many operations in the production of leather.

In what is known as the beamhouse of a tannery, where the raw skins are cleaned, dehaired and prepared for tanning, surfactants shorten the soaking time of skins and accelerate the effect of liming and deliming agents.

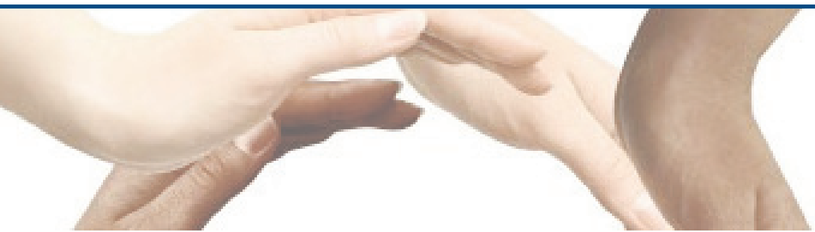
In degreasing, surfactants remove the unwanted natural fat, pave the way for tanning agents and facilitate uniform dyeing. Furthermore, they permanently soften leather or are found in “self-emulsifying” fats, which combine a fatty particle and a surfactant in a single molecule.

They are also indispensable as stabilisers of what are known as fat-liquoring emulsions for leather and in polymer dispersions for the surface finishing of leather.

Metal working, metal processing and industrial cleaning processes

Surfactants are widely used here as well. They free metal surfaces of oxide layers and fats, which is important for coating or electroplating to obtain corrosion-resistant coatings. They assist in seaming and drawing in rolling oil emulsions.

In metal processing (cutting, milling and drilling), tools need to be greased to prevent heat caused by friction. After processing, the tools must be degreased again. The coolants that are required depend on surfactants. They are used as wetting agents in metal casting and are an indispensable constituent of pickles, quenches for hardening steel, mould release agents, anticorrosion agents and oxidation inhibitors. In many cases, surfactant combinations work well instead of chlorinated solvents, which have now been



banned. There is also a constant need for surfactants in the printing industry for cleaning the rollers.

Mining

In the flotation process, surfactants are used for obtaining minerals, coal and ores from lower-content and irregular rock. In coal mining, they bind coal dust and, in the production of coal-water slurries, they enable finely ground coal to be pumped and metered like heating oil.

Petroleum industry

For reasons of environmental protection, exhaust gases from the crankcase of combustion engines are no longer discharged into the air, but recycled to the intake system for the petrol/air mixture. The exhaust gas enriched with combustion residues causes the formation of resin-like deposits in the intake channels or on the inlet valves of car engines. Such deposits can be avoided or considerably reduced by the use of selected surfactants.

In between oil changes, engine oils are exposed to high thermally oxidative stresses. The decomposition products of the oil must remain in dispersion the whole time and must not become deposited on the metal walls or in the oil filters. Surfactants and dispersing agents make a decisive contribution here. Modern multigrade engine oils would not be conceivable without such additives.

Pharmacy and health care

Surfactants are needed for the production of creams, lotions, drops, syrups, suppositories and capsules. They are necessary for processing oil-soluble or water-insoluble substances for the production of various forms of pharmaceuticals. In many cases, they have a positive effect on the release of the active substance.

The wetting properties of surfactants are important for tablets: they have to be wetted for the dispersion of the active substance in the digestive tract.

Plastics

The production of dispersions and certain plastics such as PVC would not be possible without surfactants. Two processes can be used to produce PVC polymers from VC monomers: emulsion and suspension polymerisation. In the first process, the monomers are dissolved in water together with initiators of polymerisation using surfactants. The resulting polymer forms a dispersion (emulsion). In the second process, the water-insoluble monomer is suspended in water using surfactants. The resulting polymer is beaded.

Surfactants play an important role in the production of foam plastics and thus make advances in thermal and sound insulation possible. Surfactants help to stabilise plastic dispersions, produce microcapsules and act as mould-release agents in plastic processing.

Pulp and paper industries

Surfactants disperse the resinous constituents of cellulose or lignin. They increase the softness and absorbency of paper, which is particularly critical in hygiene products (for example paper tissues). Surfactants keep screens and suction rollers clean and ensure that paper machine run smoothly. When wastepaper is being recycled, surfactants make certain that the printing ink is removed, thus preparing the paper for reuse.

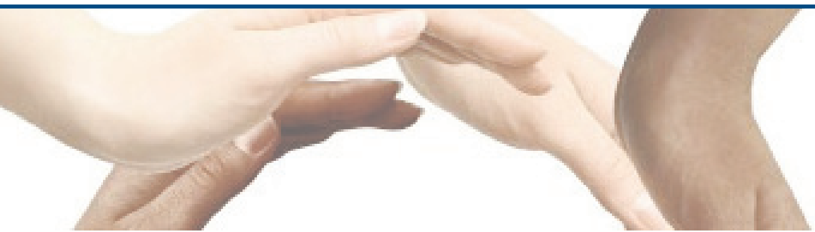
Textile and fibre industries

Surfactants find wide application in the textile industry as detergents and cleaning agents, for degumming raw silk, for fulling wool, as defoamers in various process steps, and for emulsifying and dispersing oils and waxes. Surfactants fulfil specific functions in preparing fibres and in sizing yarns, for example as smoothing agents, antistatics and adhesives. In washing synthetic fibres, the applied preparations and sizes are emulsified and dispersed to prevent spots in further processing steps, such as dyeing.

After weaving, surfactants promote the rapid soaking of the fabric and thus make it possible to swell and quickly degrade the size. In pretreating cotton, they ensure that textile-finishing chemicals have a uniform effect and thus improve the uniformity of dyeing and printing. Surfactants facilitate the use of very fine-grained dye pigments. This makes more economic use of textile colourants and simultaneously reduces residual amounts, thus lowering the impact on the environment. In dyeing, surfactants act equally as foam-free wetting agents for uniform impregnation, have a levelling effect in the dyeing process and disperse non-fixed dye during subsequent soaping to improve fastness properties.

Surfactants also provide valuable help in the finishing processes that follow the dyeing process. They are found in a large number of textile finishes such as reviving agents and flameproofing and waterproofing agents.

The development of fully synthetic fibres gave rise to a need for completely new dyeing and finishing processes. Here, surfactants played a significant role. Faster machines for spinning and twisting called for a reduction of electrostatic charges and fibres with particularly good slip and adhesion properties. Surfactants provided the solution. The needles of extremely fast industrial sewing machines get so hot sewing more than 100 stitches a second that they burn holes in the material. The use of surfactants can prevent this because they make the fibres in the fabric so smooth that they are able avoid the needle with lightning speed and with hardly any friction.



Surfactants – environmental and consumer relevance, environmental policy consequences and industry strategies

This chapter only describes the landmarks achieved in improving the environmental impact of surfactants and their human compatibility from 1960 to date. Questions of biodegradation have been of central interest right from the beginning. Numerous other activities have been developed since the 1990s to conduct risk assessments of surfactants for humans and the environment. With the entry into force of the European REACH Regulation in 2007 (Regulation (EC) No 1907/2006), a comprehensive testing programme was established by law as mandatory for all substances manufactured or used in the EU at or above one tonne per year and per manufacturer or importer. REACH stands as an acronym for **R**egistration, **E**valuation and **A**uthorisation of **Ch**emicals.

This EU law will be implemented in several stages by 2018. Furthermore, a great number of activities are aimed at quantifying or enhancing the sustainability performance of surfactants. This includes the assessment of surfactants for their CO_2 footprint, which will be outlined briefly at the end of this chapter. However, the ecological footprint of surfactants is actually very small when compared with that of heating the water required for washing or taking a shower. Surfactants reduce CO_2 emissions most effectively at low cleaning temperatures.

1. Environmental impact of surfactants

Surfactants are widely used because of their surface activity and the properties that result from this. However, damage to organisms may occur since their tension-reducing effect also influences biological surfaces. For example, adding surfactants to a lake reduces the water’s surface tension. This interferes with the exchange of air, disturbing the oxygen uptake by fish.

This aquatic toxicity plays a decisive role in assessing the environmental compatibility of surfactants because surfactants are often flushed into the wastewater after their intended use. This wastewater is usually then introduced into a biological wastewater treatment plant. After treatment, the biologically treated wastewater is generally discharged into surface waters such as rivers and lakes. In order to be able to guarantee the environmental compatibility of surfactants, it has to be ensured that surfactants do not exceed concentrations in surface waters that might pose a short-term or prolonged danger to the organisms living there, no matter whether these are bacteria, plants or animals.

Biodegradation is the most important process for removing surfactants and other substances that humans have introduced into the environment from (waste-) water (and also from soils). Therefore, ready biodegradability of surfactants is the prerequisite for guaranteeing the environmental compatibility of surfactants, i.e. the

condition that has to be met to ensure that the level of surfactants in surface waters reliably remains below the ecotoxicological threshold for water organisms.

The biodegradation of an organic substance, for example of a surfactant, is a natural process that is induced by microorganisms such as bacteria or fungi. They transform the organic substance into endogenous substances in a multistage process controlled by metabolic enzymes or degrade them to simple inorganic compounds such as carbon dioxide, water and possibly inorganic salts (simplified: mineral salts). Microorganisms use organic substances as an energy or carbon source for their vital processes and for the formation of new biomass or use them as a source of essential (nutrient) elements (nitrogen, phosphorus and sulphur).

European legislation on the biodegradation of surfactants

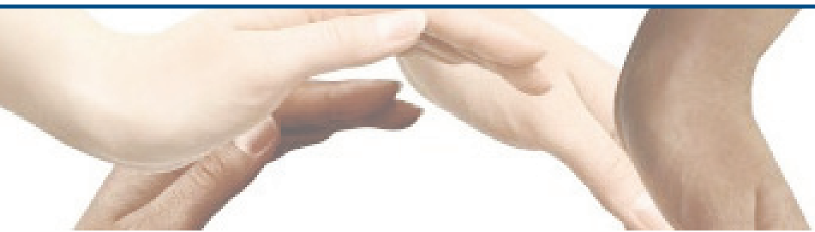
Biodegradation of a surfactant is a multistep process that generally takes place in the presence of (atmospheric) oxygen (and thus under what are known as aerobic conditions).

The first step of degradation is referred to as **primary degradation**. Surfactants lose their surface activity and thus their typical characteristics. Since toxicity to aquatic organisms is associated with this surface activity, primary degradation leads to a substantial decrease in the toxicity of most surfactants.

In further degradation steps, the product of primary degradation is subsequently broken down into ever smaller and simpler intermediates until finally all structural elements of the initial compound have been converted into carbon dioxide, water, inorganic salts and biomass (bacterial cell mass). This is called **final or ultimate degradation**.

A surfactant is regarded as **readily biodegradable** if it attains or exceeds a certain threshold, i.e. pass level (see also explanations of screening tests and method descriptions in the Annex).

Since primary degradation substantially decreases the aquatic toxicity of most surfactants, it has been of great relevance to the environmental compatibility of surfactants. Therefore, in the past, legislation in most European countries only required primary biodegradability for the groups of surfactants mainly used in detergents and cleaning agents, i.e. anionic and non-ionic surfactants. As early as 1964, German law required a minimum primary biodegradability of 80% for anionic surfactants in detergents and cleaning agents. This primary degradation is what is meant by the statement “at least 90% biodegradable”, which often refers to surfactants in consumer products. As a result of European integration, environmental and water protection has long been a European matter. The biodegradability requirements for surfactants used in detergents and cleaning agents have been tightened in several steps with the aim of recycling all chemical elements of a surfactant in the natural material cycle. Today, European Regulation EC No 648/2004 on detergents, which came into force on October 8, 2005, is valid throughout the EU. This regulation only allows the use of readily biodegradable and thus completely degradable surfactants.



The first impetus for the development of today's standard surfactants came in summer 1959. At that time, large amounts of foam were accumulating on the water surface mainly at weirs and locks. The cause – a poorly biodegradable detergent surfactant – was immediately removed from the market and the use of this group of surfactants banned by law.

Thus, a surfactant not only led to the Federal Republic of Germany becoming a pioneer in environmental legislation, but also triggered a systematic change that has decisively influenced this group of chemical substances since then. The compatibility of surfactants with water and the organisms living in it has steadily been optimised while maintaining and improving their positive properties. As a positive result, today's surfactants are a new generation of chemical substances.

Through a more conscious use of surfactants in formulations and products as well as advanced wastewater treatment technology, surfactants have become impressive evidence that an environmental problem can be eliminated. Together with scientific institutions as well as national and EU authorities, industry has shown that international cooperation is possible for the benefit of the environment. The following sections will clarify this further.

Test procedures for the environmental impact of surfactants

Comprehensive scientific instruments are now available for examining the degradation behaviour of surfactants. The objective of all of these procedures is to be able to compare the measured values. In addition to simple standardised test procedures (screening tests), there are considerably more sophisticated standardised wastewater treatment simulation tests, which establish the scope of surfactant biodegradation under conditions as realistic as possible. Ecotoxicological studies provide evidence of the effect of surfactants on aquatic organisms. In a first step, they start by determining the short-term (acute) effects on important members of or links in the aquatic food chain, such as bacteria, algae, freshwater crustaceans (daphnia) and fish. Based on these data, studies of prolonged toxicity (subchronic/chronic effect) to the individual groups of organisms are carried out. In particular, the highest test concentration is determined at which effects are no longer observed as compared with controls (no observed effect concentration = NOEC). According to present knowledge and taking safety factors into account, a reliable prediction of the substance concentration at which effects are no longer observed in the environment (predicted no effect concentration = PNEC) can be established from all these investigations. For particularly interested readers, these associations between the actual substance concentration (predicted environmental concentration = PEC) and a "tolerable" substance concentration (PNEC) will be explained in more detail in the following section.

Environmental risk assessment of surfactants – test data, safety factors and PEC/PNEC ratio

Under the Regulation on the evaluation and control of the risks of existing substances (EC No 793/93), which was revoked when REACH came into force (see below), the European Union (EU) established a testing programme for chemicals many years ago to detect whether chemical substances pose hazards to the environment. The technical term for this is: Environmental Risk Assessment.

The following conclusion can be drawn by comparing surfactant concentrations in running waters that are determined by environmental monitoring programmes and studies or predicted using computer models (predicted environmental concentration = PEC) with PNEC (predicted no effect concentration) values based on

ecotoxicological studies: today's commonly used surfactants do not pose any risk to organisms in aquatic environments based on current information. However, the good degradation properties of surfactants have to be effective when wastewater is purified in biological wastewater treatment plants.

The following risk assessment procedure is commonly used today:

When determining the predicted environmental concentration of a chemical (**PEC**), experimental data on biodegradability as well as consumption rates, dilution effects, exposure-relevant physicochemical parameters (for example volatility, i.e. escape into the air), adsorption capacity to surfaces (adsorption to sewage sludge) and relevant boundary conditions are considered to obtain a value that is as close as possible to the actual substance concentration on site. Accordingly, the leading question is: what amounts of a certain surfactant enter into the environment after use and at what concentration?

To calculate the predicted no effect concentration below which exposure to a substance is not expected to cause adverse effects to species in the environment (**PNEC**), the **NOEC** values derived from ecotoxicological tests are divided by a safety factor. Different safety factors are applied depending on the type and number of ecotoxicological test data obtained. The greater the number of studies, the lower the safety factor used for deriving the PNEC from the available data. For example, if acute toxicity levels are available from three test organisms (fish, daphnia and algae), the PNEC is determined by dividing the lowest acute toxicity level by a (safety) factor of 1,000. However, if NOEC data are available for three different types of organisms from chronic toxicity tests (and thus higher quality information as compared with that from acute toxicity tests), the PNEC corresponds to one tenth of the NOEC of the most sensitive organism. After the PEC and PNEC have been calculated, a comparison is made based on the quotient of PEC and PNEC. If the PEC/PNEC quotient is smaller than 1.0, this surfactant is not expected to cause any toxic effects on organisms.

A monitoring study that was carried out in the Netherlands in 1995 measured concentrations of the standard surfactant LAS (linear alkyl benzene sulphonate) and the other main surfactants at that time, i.e. fatty alcohol ethoxylates (FAEO) and fatty alcohol ether sulphates (FAES) in the effluent from seven wastewater treatment plants. On the basis of these measured effluent concentrations, PEC values that considered the dilution of the effluent in water and the expected elimination were determined for these surfactants.

Here, too, a comparison with the PNEC values demonstrated that these surfactants reliably posed no hazard to the aquatic environment if wastewater was treated according to current technology.

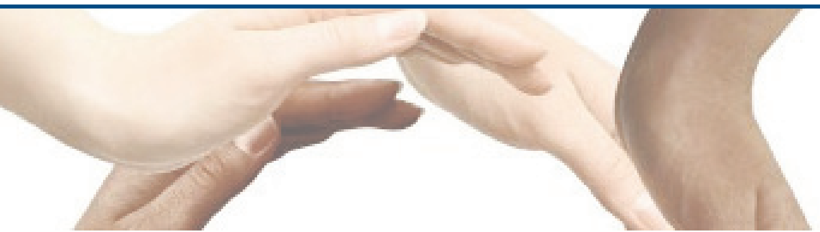


Table:

Group of surfactants	*PEC [µg/l]*	*PNEC [µg/l]*	*PEC/PNEC*
LAS	5	30	0,2
FAEO (C_{12}-C_{15})	0,5	10	0,05
FAES (C_{12}-C_{15})	1,2	10	0,1

Average PEC and PNEC values (PNEC = NOEC x 10^{-1}) and PEC/PNEC ratio for various groups of surfactants based on measurements from seven wastewater treatment plants in the Netherlands (carried out in 1995)

Studies of the degradation behaviour of LAS (linear alkyl benzene sulphonate)

In the 1990s, ecological studies of surfactants paid particular attention to the residual amounts of the standard LAS surfactant detected in the oxygen-free digested sludge from municipal wastewater treatment plants. Test results have confirmed that LAS is degraded rapidly and completely in water – in the presence of oxygen and thus under aerobic conditions. The question that then arises is whether this is also the case in the soil if sewage sludge is used as a fertiliser or soil conditioner in agriculture. All previous results have suggested that degradation in the soil in the presence of oxygen proceeds just as fast as in water. Generally, the question of possible accumulation in water organisms (bioconcentration) also plays an important role for the assessment of risks posed by chemical compounds. ERASM (Environmental Risk Assessment and Management), a research initiative created by the European industrial associations A.I.S.E. (Association de la Savonnerie, de la Détergence et des Produits d’Entretien) and CESIO (Comité Européen des Agents de Surface et de leurs Intermédiaires Organiques) in 1991, has obtained test results on samples of surfactants suggesting that LAS is also readily degraded in animal organisms and therefore does not accumulate there.

The behaviour of LAS in an anaerobic (i.e. oxygen-free) environment remained a controversial matter for a long time. In 2000, the European Commission’s Directorate-General for Enterprise and Industry had entrusted the Fraunhofer Institute for Environmental, Safety and Energy Technology (UMSICHT) with an assessment of the environmental impact of an incomplete anaerobic degradation of surfactants. The Fraunhofer report submitted in 2003 met with objections by the EU Scientific Committee on Health and Environmental Risks (SCHER). The statement published by SCHER in November 2005 criticised the insufficient database of the Fraunhofer report, but nevertheless endorsed its estimate that LAS in sewage sludge does not give cause for concern. As a result, CESIO commissioned additional studies at the National Environmental Research Institute in Denmark to clarify any unanswered questions. These studies demonstrated that the PEC/PNEC ratio of LAS remained below one in all environmental media (surface waters, wastewater treatment plants, sediments and soils).

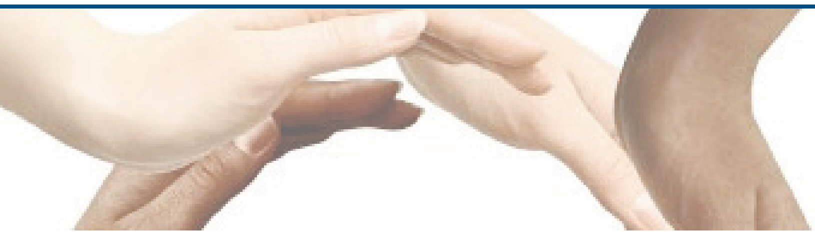
In 2007, the European surfactant manufacturers under the joint HERA research project (see section below) published a comprehensive assessment of the use of LAS based on the Danish studies. The HERA report has concluded that LAS pose no hazards to either the environment or health. Although SCHER also objected to this report with regard to its methods and the studies on which it was based, it agreed with the general conclusions as to health and environmental hazards. A final report from the EU Commission to the European Parliament and the Council (COM(2009) 230 final) published in May 2009 concerning anaerobic biodegradation pursuant to Article 16 of Regulation (EC) No 648/2004 on detergents concluded: *"Following a systematic evaluation of the risks from the presence of non-degradable surfactants in various anaerobic compartments, it was concluded that, in contrast to the adverse effects observed in the absence of aerobic degradation, the lack of anaerobic degradation does not seem to be correlated with any apparent risk for these environmental compartments. It can therefore be concluded that anaerobic biodegradability should not be used as an additional pass/fail criterion for the environmental acceptability of surfactants such as LAS which are readily biodegradable under aerobic conditions."*

2. Detergents and cleaning agents: risk communication along the supply chain

In 1999, the European associations of the detergent and chemical industries initiated a joint project for a faster, systematic assessment of detergent components. Under a project called HERA (Human and Environmental Risk Assessment of ingredients of household cleaning products) that was initially limited to five years, risk assessments were carried out for the most important detergent components. The objective was to develop an assessment strategy that was based not only on hazard data but also considered the risk of a product for the end user as early as possible. In this way, the potential effects on consumers became the focus of interest in addition to the environmental risks. It specifically addressed the assessment and labelling of the health and environmental risks associated with the use of surfactants in private households. Another objective of HERA was to develop a risk assessment procedure that could be carried out quickly and that paved the way to new assessment strategies that were based on real conditions to a greater extent than before.

For the safe handling of detergents and cleaning agents, consumers specifically need information on the proper dosing and handling of household products containing surfactants. Therefore, the main focus of HERA was risk communication along the supply chain, ranging from raw materials producers to processors and finally to end users. Stakeholders such as environmental and consumer protection associations were also included.

HERA was a two-phase project. A common method was developed in the first phase of



HERA, which was used in phase 2 as a basis for carrying out the risk assessments covering all relevant groups of chemical constituents and all exposure scenarios for humans and the environment. Altogether, more than 250 substances used in detergents and cleaning agents were investigated and evaluated. On completion of the studies, the results of the risk assessments were published successively on the Internet under www.heraproject.com. It turned out that five years were not sufficient for a total evaluation since some assessments were not completed before 2009 or 2010. The activities of industry associated with HERA laid important groundwork and provided the basis for the risk analyses and assessments of chemical substances required under the new European chemicals legislation (REACH).

3. The new European chemicals legislation (REACH)

The European surfactant manufacturers benefitted from the experience they gained under the HERA project for the implementation of the new European chemicals legislation that came into force in June 2007. In 1999, the European environmental ministers initiated the legislative process for this regulation with the aim of improving the database on all substances produced and used in the European Union and of ending the varying assessment of existing substances and new substances that had been introduced after 1981. Only the latter had been subject to a uniform and systematic risk assessment and registration procedure. All chemicals that were placed on the market before 1982 are now required to undergo a systematic review and risk assessment. The following principle applies: “No data – no market.”

This means that it is no longer possible for any substance to be placed on the EU internal market without data being submitted on health hazards and environmental risks that were obtained by standardised test procedures. However, there are justified exemptions to the registration requirement for substances known to be harmless and for substances such as medications or food and feedstuffs whose risk potential has been assessed through specific statutory provisions. Exemptions currently still apply to polymers (chain molecules) that comply with the definition of polymers under REACH. They do include quite a number of surfactants, but many are not exempted. In addition, monomers required for the manufacture of polymers – and this also applies to imported polymers – have to be registered under REACH if they exceed a certain total quantity. This gives an idea of the challenges that the affected companies are facing in implementing REACH.

Nevertheless, the surfactant industry has every reason to believe that it will also be able to successfully tackle this challenge on the basis of its many years of experience with risk assessment, risk management and risk communication.

The statutory requirements that are placed on the manufacture, nature and environmental behaviour of substances have meanwhile been exceeding classic life cycle assessments. Climate policy requires both evidence of toxicological safety and a minimisation of the carbon footprint, i.e. the ecological footprint of sub-

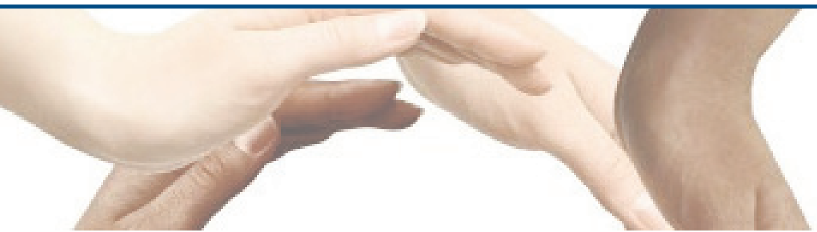
stances or manufactured products under the aspect of climate protection. The total consumption of energy and material required for the production of raw materials and products is converted to CO_2 equivalents to assess their possible theoretical influence on the average temperature over the land masses of the earth.

4. The ecological footprint (Life Cycle Assessment 2.0)

For a comprehensive assessment of the environmental relevance of a substance, all influences and impacts ranging from raw material production to its use and disposal need to be recorded. Here, the climate protection debate has required a parameter that allows a definitive statement to be made about a product's impact on the climate. This impact is expressed in CO_2 equivalents and has finally made it possible to compare products in terms of their CO_2 footprint.

A life cycle inventory study from the early 1990s, which was carried out by ten European surfactant producers, is used to address such concerns. Here, specific "cradle to factory gate" studies were carried out for important groups of surfactants (including the above-mentioned LAS, FAEO and FAES). Any manufacturer may use the results of this life cycle inventory analysis as a potential to improve the environmental profile of its production processes and the resulting end products. This applies to both surfactant-specific process steps and general factors necessary for chemical production, such as the provision of electricity, fertilisers, auxiliaries and transport capacities. These would have to be supplemented by the CO_2 effects associated with manufacture and use.

The surfactant industry is currently updating its earlier life cycle inventory studies to include the CO_2 footprint.



Surfactants and renewable raw materials

The term “renewable raw materials” refers to raw materials produced in agriculture and forestry that are used as materials themselves or as an energy source apart from food and feed production. Fossil raw materials are their counterparts. They include coal, crude oil and natural gas. These are raw materials that presumably developed wholly or in part from the decomposition of dead plants or animals far back in Earth’s history. Unlike these materials, which can only be renewed – if at all – over long geological periods, renewable resources can regenerate on a yearly basis or in periods that are foreseeable from a human perspective.

Renewable raw materials for the manufacture of surfactants

Both fossil and renewable raw materials are used for the manufacture of surfactants. Some surfactants, such as linear alkyl benzene sulphonates (LAS), can be produced only on the basis of fossil raw materials, i.e. primarily crude oil. Benzene and long-chain alkanes are the raw materials in this case. Other surfactants, such as alkyl polyglucosides (APG), are entirely made of renewable resources. The raw materials used in this case are starch (as a source of glucose) for the hydrophilic end of the molecule and coconut oil (as a source for the second component, i.e. fatty alcohol) for the hydrophobic end.

Still other surfactants are produced using both fossil and renewable raw materials. One such example are fatty alcohol sulphates: their production is based on fatty alcohols that are converted to fatty alcohol sulphates by reacting with a gaseous sulphur trioxide/air mixture and then being neutralised with a sodium hydroxide solution. Of the approximately 2 million tonnes of fatty alcohols that were produced worldwide in 2003, about 50 per cent were made from renewable raw materials, 45 per cent from crude oil and 5 per cent from coal.

Surfactants containing at least one constituent derived from renewable raw materials now have an about 50 per cent share of the total surfactant market in Europe. A position paper submitted by four chemical associations in early 2010 entitled “Change in the Raw Materials Base” (www.dechema.de) points out that more than one third of industrially processed plant fats and oils are used for the manufacture of surfactants. The ratio between synthetic and natural sources in the manufacture of fatty alcohols has considerably shifted in the past 30 years. Whereas it was 60 to 40 in 1980, today it is exactly the other way round. This shift is only slightly due to the politically desirable displacement of crude oil by plant oils and fats. Instead, cost considerations were the main reason why chemists took increasing advantage of the gratuitous synthesis efficiency offered by plants.

Arguments in favour of the manufacture of surfactants from renewable raw materials – a critical assessment

One might jump to the conclusion that the use of renewable raw materials is per se better than the use of fossil and thus finite resources. Let us take a closer look at the arguments in favour of renewable raw materials to get a balanced view:

Does the use of renewable raw materials contribute to conserving finite fossil resources, such as crude oil, natural gas and coal?

It is undisputed that the conservation of fossil resources is necessary since crude oil and natural gas are non-renewable raw materials in

the medium term, i.e. what is consumed today is no longer available to future generations.

However, even renewable raw materials cannot be used indefinitely. The Earth's arable regions are limited and their sustainable cultivation is no matter of fact (soil leaching and erosion).

Furthermore, it has to be borne in mind that only about 0.1 per cent of crude oil consumed each year is used for the manufacture of surfactants, whereas about 93 per cent of crude oil consumed each year is used for energy production and traffic. Thus, even a complete substitution of crude oil-based surfactants – which is only theoretically conceivable – by native surfactants would provide a hardly perceptible contribution to the conservation of resources. In view of the technical and economic difficulties that would result, it remains questionable whether this currently makes sense. A life cycle analysis that includes the use of the surfactant is a good tool to assess sustainability.

In most cases, the conservation of resources was not the main reason why renewable raw materials such as coconut or palm kernel oil began to be used for the manufacture of surfactants. A more important factor was the greater availability of the medium-chain-length fatty acids (between 10 and 14 carbon atoms) that these plant oils contain and that are important for surfactant production.

Are surfactants from renewable raw materials CO_2 neutral?

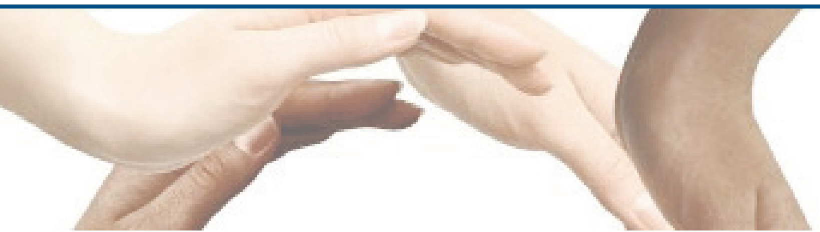
Surfactants from renewable raw materials are more or less CO_2 neutral if landscape alterations such as rainforest clearing and drainage of moorland and peatland are not taken into account. Ultimately, a life cycle inventory analysis is a suitable tool for establishing a CO_2 footprint. Therefore, the surfactant industry is currently updating its earlier life cycle inventory studies to include the CO_2 footprint. However, the use of renewable raw materials by the chemical industry in general and for the manufacture of surfactants in particular is only a small step to solving the CO_2 problem since the amounts currently used are too small. An increase resulting from an almost complete replacement of fossil raw materials by renewable ones is not always possible or useful, at least not if positive secondary effects are taken into account. Secondary effects here refer to energy savings and thus reductions in CO_2 emission that can be achieved using surfactants to optimise processes. This includes lowering the washing temperature (30°C wash) or reducing friction loss in pipelines. Since the CO_2 saving potential of secondary effects is often considerably higher than that of primary substitution, it has to be ensured that substitution is not obtained at the expense of poorer technical performance. The cited LAS example shows that in some cases it is not possible to replace a petrochemically based surfactant by a native surfactant.

Are surfactants from renewable raw materials (more readily) biodegradable?

Supporters in favour of using renewable raw materials often also argue that surfactants from renewable raw materials are more readily biodegradable than surfactants produced from fossil raw materials.

The origin of the raw material is however not relevant to the biodegradability of a substance; instead, the chemical structure of the molecule is decisive. For example, defined fatty alcohol sulphates based on fossil raw materials show the same degradation behaviour as fatty alcohol sulphates that were produced on the basis of renewable raw materials.

Nevertheless, practice has shown that all surfactants from renewable raw materials are readily biodegradable since they have only linear



carbon chains that pose no problem to microorganisms. Among surfactants from fossil raw materials, there are definitely some representatives that are equally readily degradable, such as those with lightly branched alkyl chains. Very highly branched chains, however, often show insufficient degradability – microorganisms are not familiar with such chains from their natural habitat.

However, surfactants with branched chains have other technical characteristics that surfactants with linear chains do not have. Since surfactants with branched alkyl chains are generally more readily soluble, more highly concentrated liquid products can be manufactured. This is of advantage for transport and storage. Therefore, it is not possible to simply substitute surfactants from fossil raw materials by surfactants from renewable raw materials.

Is the manufacture of surfactants from renewable raw materials less harmful to the environment?

Renewable raw materials are often grown in monocultures, which require an increased use of fertilisers and crop protection products. The areas necessary for their cultivation are often obtained by clearing natural forests. This may lead to a reduction of biodiversity unless the areas are reforested. Approaches have been developed to sustainably cultivate oil palm plantations. Within the Roundtable on Sustainable Palm Oil (RSPO), some European palm oil traders and processors have committed themselves to buying only palm oil that was examined and certified as being “sustainable” in cooperation with the World Wide Fund for Nature (WWF) and its partners.

Are surfactants on the basis of renewable raw materials milder to the skin and therefore more suitable for use in the cosmetic industry?

Surfactants from renewable raw materials are generally not more suitable for the manufacture of cosmetics than synthetic surfactants. Many irritants and toxicants also exist in nature. Some of them are far more toxic than any toxin made by human hand. However, especially high-end products of the cosmetic industry are based on synthetic compounds.

The above answers to typical questions comparing surfactants on the basis of petrochemical raw materials with those of renewable origin reveal that it is the surfactant molecules with their chemical structures themselves that are ultimately responsible for the assessment rather than the origin of the raw materials. This requires an objective discussion of the issues – always in the light of the intended applications. For many years, the surfactant industry has gained experience using different raw material sources and has found ways of developing combinations that are effective and resource-efficient while taking product optimisation into account.

In summary, both surfactants on the basis of renewable raw materials and those on a petrochemical basis can be used equally well. Depending on what characteristics are desired and which assessment criteria are used, both groups of raw materials have advantages or disadvantages vis-à-vis each other.

Prospects

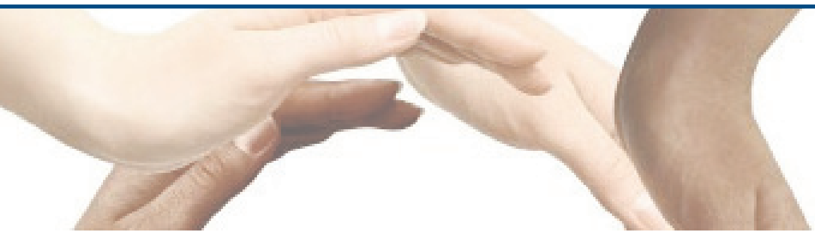
Important economic factors

Surfactants enable us to manufacture efficiently, use innovative procedures and develop globally competitive products. Discontinuing the use of surfactants would amount to a step back to the pre-industrial Stone Age. At the same time, we would be poorer in terms of many proven solutions and lose the chance of solving important current and future problems, such as how to save energy, use our fossil energy reserves more efficiently and protect our health.

The environmental problems that surfactants caused in the past have rapidly been solved. The cooperation between legislation, authorities and industry focussed on mutual success, and this has proved its worth. Moreover, industry solved problems that were likely to occur on its own, even before legislative measures were necessary. This self-imposed commitment to developing not only more efficient and more economic, but also increasingly environmentally safe surfactants is clear evidence of industry's willingness to take responsibility vis-à-vis humans and all of nature.

Industry will continue to give priority to environmental protection in the development of its products with a strong focus on research and investment and will remain a reliable partner of the scientific community, authorities and users.

The possibilities of modern surfactants and the potential for tailor-made problem solutions and intelligent combinations have yet to be exhausted. Perspectives based on nanotechnology are currently emerging, but are still controversial. Here, the distinctions between chemistry and physics are no longer as clear-cut since the characteristics of particles with a diameter that is roughly equal to one billionth of a meter no longer depend on their chemical composition, but primarily on their size. This makes it possible to avoid using biologically and ecologically problematic chemicals right from the beginning. However, environmentalists fear that this progress will necessarily mean accepting new and currently still largely unknown risks. These concerns have to be taken seriously. It is obvious that there is no such thing as an ultimate solution, both as regards one's personal life and as regards technology and the economy. There will always be new findings and data to challenge tried and tested ones and to open new ways and perspectives.



Annex
Environmental compatibility testing

Test procedure: How is biodegradability tested?

The biodegradability of organic chemical substances is officially tested by means of standardised test methods that are required by law. These test methods ultimately show whether a substance can be classified as “readily biodegradable”. This parameter is determined by means of screening tests (and if necessary, inherent and/or simulation tests). It is used for a preliminary assessment of organic substances and is for example relevant to the EU classification “dangerous for the environment”, the EU Detergents Regulation that came into force on October 8, 2005 and the German Chemicals Act.

(1) Screening tests

Screening tests (OECD 301 A-F) are simple static laboratory tests resulting in relatively stringent assessments. For practicability and cost reasons, such screening tests are often initially used to test the biodegradability of a surfactant.

In these tests, small amounts of the surfactant are dissolved once in a test vessel containing a solution of water and mineral salts. This solution is inoculated with small amounts of a microorganism mixture. The microorganisms are generally derived from the effluent of a municipal wastewater treatment plant or from river water. Their diversity thus corresponds to the microorganisms present in the aquatic environment. In the solution, the added surfactant is their sole source of carbon or energy.

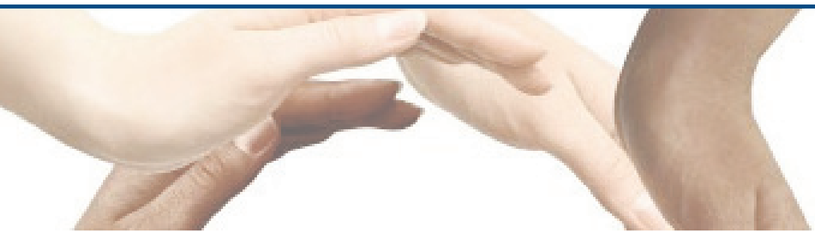
After the surfactant and microorganisms have been added, the test vessel is loosely sealed and kept at 25°C for a maximum test period of 28 days and shaken to provide oxygen, which the microorganisms require for degradation.

Samples are removed at fixed regular intervals, and the degradation rate of the surfactant is determined by means of suitable analytical methods.

Analytical parameters

Depending on the test method, three different analytical parameters can be used to measure the extent to which the tested surfactant has been removed from the environment.

1. **Decrease in test substance/surfactant**
   by determining the dissolved organic carbon (DOC) in the liquid culture medium.
   The more the surfactant can be utilised/degraded by bacteria, the greater the decrease.
   (In addition to biodegradation, the removal of organic substances from (waste-) water can be recorded physically or chemically, e.g. by adsorption to sewage sludge or precipitation when measuring the DOC.)



2. **Biochemical Oxygen Demand BOD**
   Microorganisms consume oxygen O_2 (oxidative degradation) while a surfactant is being degraded. Therefore, in (aerobic) surfactant degradation, the consumption of dissolved, free oxygen by microorganisms – the **B**iochemical **O**xygen **D**emand **BOD** – provides information about the degradation rate of the surfactant.
   The degradation rate is obtained by comparing the measured BOD with the theoretical oxygen demand (ThOD) required to degrade the test substance completely. Instead of the calculated ThOD, the experimentally determined oxygen demand is often used for the complete chemical oxidation of the test substance, the **C**hemical **O**xygen **D**emand **COD**.
3. **CO_2 formation in degradation**
   CO_2 is formed as a “waste product” during the degradation of surfactants.
   Therefore, the amount of CO_2 formed reveals the degradation rate of the surfactant. Here, too, the degradation rate is obtained by comparison with a suitable reference value.

If a screening test that is based on a specified method and test period shows that the degradation of a surfactant attains or exceeds a certain threshold, i.e. pass level, the surfactant is considered to be readily biodegradable.

Pass level according to the EU Detergents Regulation

The reference method for the laboratory testing of the complete biodegradability of surfactants under the Detergents Regulation is based on ISO Standard 14593: 1999 (CO_2 headspace test). Surfactants in detergents are considered to be biodegradable (according to EU Regulation (EC) No 648/2004) if the rate of degradability (mineralisation) is at least 60 per cent within 28 days.

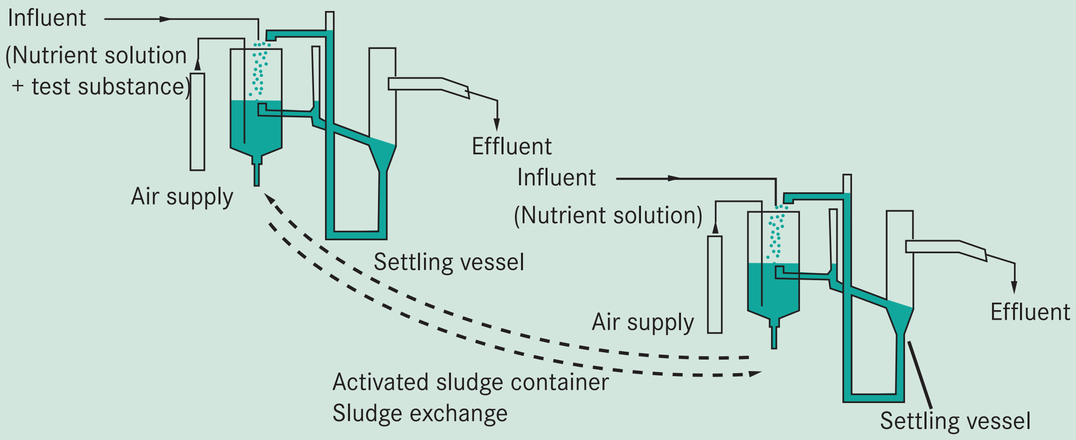
Depending on the physical properties of the surfactant, other methods may also be used (DOC die-away test or modified OECD screening test). A biodegradability rate of 70 per cent within 28 days is considered to be of equal value using these methods.

If the relevant pass level is reached, the tested surfactant is regarded as readily biodegradable under environmental conditions. However, if a surfactant does not attain the pass level stipulated by the Detergents Regulation, the manufacturer of detergents that contain such a surfactant and that are intended for industrial or institutional use may apply for an derogation. If the detergent is intended for other uses or if the application for derogation is rejected, the detergent containing the specific surfactant may no longer be placed on the market.

(2) Simulation tests

Simulation tests are methods of testing the degradation behaviour of surfactants under conditions close to reality. The activated sludge simulation test (OECD 303 A) is the most important simulation test method in practice. It simulates the biological treatment operation stage of a wastewater treatment plant on a laboratory scale (see also box). To recreate the conditions in a real wastewater treatment plant, it uses relatively low surfactant, but high microorganism concentrations. In addition to the tested surfactant, synthetic or municipal wastewater is added **continuously (→ dynamic procedure!)**. In this way, microorganisms are supplied with different organic compounds (C sources and energy sources!) that they can degrade – as under wastewater treatment plant conditions.

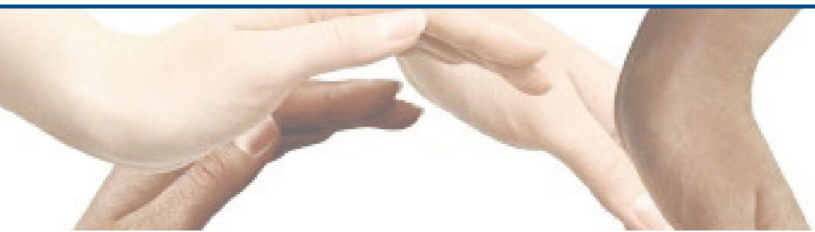
OECD 303 A: Coupled units test



Source: Wagner: “Waschmittel – Chemie und Ökologie” p. 108

A large number of microorganisms are present as activated sludge in every laboratory-scale wastewater treatment plant model (biological treatment stage). The surfactant to be tested is continuously added to one of these wastewater treatment plant units together with a large excess of readily biodegradable organic compounds (synthetic or municipal wastewater; in the figure: nutrient solution and test substance). This simulates natural conditions where microorganisms can degrade different organic compounds.

The second plant model consists of a control wastewater treatment plant that contains only synthetic wastewater without any surfactant to be tested. Otherwise, the two laboratory-scale wastewater treatment plants work in the same way. A dosing pump (not shown) continuously



supplies the solution to be tested. It is adjusted in such a way that the test solution and a fraction of the activated sludge pass through the activated sludge container of the plant within three hours. Another pump ensures that the microorganisms in the activated sludge container are supplied with a sufficient amount of oxygen for the degradation of both surfactant and the other readily biodegradable organic compounds that have been added (in figure: air supply). The effluent of the activated sludge container is collected in a settling vessel in order to separate the activated sludge by sedimentation. The activated sludge is then pumped back into the activated sludge container.

The dissolved organic carbon concentration, i.e. DOC level, is regularly measured in the influent and effluent of the two laboratory-scale wastewater treatment plants. The degree to which the tested surfactant has been degraded is established by contrasting the results measured in the two plants.

The sludge is exchanged at regular intervals to provide a comparable biological basis. Hence the name of this test is coupled units test.

(3) Inherent tests – tests to determine “basic degradability”

This group of tests is used to test general (potential or inherent) degradability, mainly of surfactants that are not subject to the Detergents Regulation.

These tests record biodegradation as well as physical and chemical processes for the removal of the surfactant from (waste-) water (evidence of DOC decrease (see box)). The Zahn-Wellens test (OECD 302 B) is primarily applied in Germany. Like the screening test, it is a static procedure, but uses high bacterial and test substance concentrations (activated sludge test, but without any model character (see (3)).

Clearly positive test results suggest that the surfactant is basically degradable under wastewater treatment plant conditions and thus has no permanent impact on the environment.

However, since this test hardly differentiates between readily and only moderately degradable substances and may therefore lead to false positive rather than to false negative results, the degradation behaviour of the surfactant is tested in a simulation test if the findings are unclear. These tests are also applied if additional information is required about the degradation behaviour.

Practical relevance of laboratory degradation test results

Because of the conditions of the method used, the screening test results cannot be applied to the environment directly. However, a comparison of results from screening tests with those from simulation tests and environmental monitoring data has demonstrated that if a positive test result is obtained in the screening test, for example if there is evidence of ready biodegradability, ready and fast degradability is also guaranteed in the environment. In such a case, complete biodegradation in the environment can be assumed even if the surfactant was not completely degraded in the laboratory test.

This conclusion also applies to those fractions of surfactant that are not degraded in wastewater treatment plant simulation tests. Wastewater treatment plants have not been designed to completely degrade all organic material within the limited residence time. They are only intended to reduce the organic material load of wastewater to such an extent that degrading organisms present in natural surface waters are able to eliminate the rest without any problems. More sophisticated test methods, such as metabolite tests, may be applied if surfactant residues that were not degraded in tests still contain stable or poorly degradable intermediates.

Aquatic toxicity

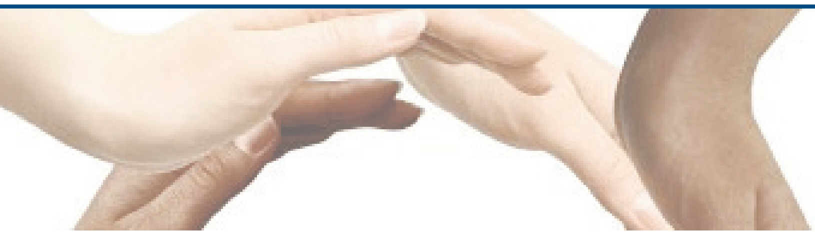
In addition to biodegradability, an environmental risk assessment of surfactants should include the evaluation of their toxicity to water organisms, i.e. aquatic toxicity.

Test methods – principles to determine aquatic toxicity

From a biological point of view, (surface) water is a habitat for a variety of different organisms. These organisms do not live in isolation from each other in bodies of water, but they are interdependent members of a community. Therefore, the impairment of one member of such a community, for example by a surfactant, may change the complete community. A simple example is to illustrate this.

When the development of unicellular algae is disturbed, daphnia (water fleas) are left without food. They cannot grow or multiply. This, in turn, means that the fish that feed on these freshwater crustaceans cannot exist either, etc.

Scientific knowledge of the complex interrelations and modes of action within such communities is still incomplete and, strictly speaking, tests for the aquatic toxicity of a substance ought to be carried out with complete aquatic communities. However, since – with few exceptions – it is not possible to simulate complete aquatic communities in a laboratory and the evaluation/assessment of these tests is difficult, tests are generally carried out with individual selected, sensitive representatives of the classic aquatic food chain that are available year-round and can easily be cultured. These are unicellular green algae as important representatives of plant organisms, daphnia (water fleas) as herbivorous animal organisms and fish (mainly zebra fish in Germany) as representatives of one of the upper levels of the food chain. Bacteria are also included in testing because



any impact on bacteria is of relevance, such as in the case of discharge into biological wastewater treatment plants. Furthermore, any impact on bacteria reduces the self-purifying capacity of natural bodies of water (moreover, they close the material cycle as destruents by remineralising (dead) plant and animal biomass).

EU or OECD guidelines require tests to be carried out with the described organisms – with the exception of bacterial tests – to determine the aquatic toxicity of a substance. Since the results are obtained in individual organisms under standard laboratory conditions, they may only indicate the hazard potential posed by a substance and cannot be applied to the environment directly.

Assessment of aquatic toxicity: acute and chronic toxicity

Both acute and chronic toxicity have to be considered when assessing the aquatic toxicity of a surfactant. Acute toxicity describes toxic effects that occur after relatively short-term contact of the organisms with the tested substance. The lethal concentration LC_{50} or the effect concentration EC_{50} is determined as the parameter (see box).

Acute toxicity

Toxic effects that occur after relatively short-term contact of the test organisms with the tested surfactant. Parameters: **LC_{50}** or **EC_{50}**

LC_{50}: concentration at which 50% of the tested individuals die (LC: lethal concentration)

EC_{50}: concentration at which certain adverse effects, e.g. growth inhibition (green algae) or change in swimming ability (daphnia) occur in 50% of the tested individuals

Determination of the LC_{50} or EC_{50} values

A certain number of selected test organisms are exposed to different concentrations of the tested substance. In this way, both the highest test substance concentration at which no lethal effects (in fish) or adverse effects on essential manifestations of life (swimming ability in daphnia or cell growth in algae) occur (LC_0 or EC_0 value) and the lowest test substance concentration that leads to acute effects on all test organisms (LC_{100} or EC_{100} value) can be determined after defined periods (48 hours in daphnia, 72 hours in algae and 96 hours in fish). The LC_{50} or EC_{50} can be calculated from these data.

Chronic toxicity describes toxic effects that occur only after prolonged contact of the organisms with the tested substance. The NOEC value is usually specified as the parameter (see box).

Chronic toxicity

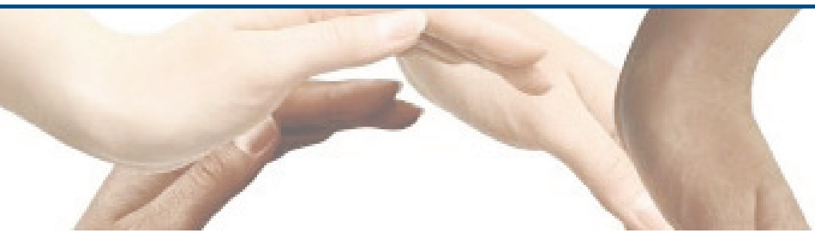
Toxic effects that occur only after prolonged contact of the organisms with the tested substance. Parameter: NOEC

NOEC: no observed effect concentration – highest concentration of the tested substance at which no adverse effects are observed

Determination of the NOEC

Like the LC or EC (see above), the NOEC is determined by means of a concentration series. However, the test periods are generally longer and the main focus is on the impact on certain manifestations of life rather than on the lethality of the substance to the test organism. For example, the impact on the growth rate of the animals is tested in daphnia, the adverse effect on swimming ability, operculum movement and feeding behaviour is tested in fish or the impact on the development of the eggs (hatching and survival rates of the embryos) and larvae is investigated in early life stage (ELS) tests. Therefore, chronic tests are clearly more sensitive than acute tests in most cases.

Tests or data on acute and chronic toxicity are relevant to classification and labelling according to the EU chemicals law. However, the assessment of the environmental risk of surfactants is based on tests of chronic toxicity or on data obtained from these tests (see also box on the validity of the relevant parameters.)



Glossary

Aerobic
Conditions characterised by the presence of oxygen. Mode of life of animal and plant organisms requiring oxygen for respiration

Agglomeration
Accumulation or aggregation

A.I.S.E.
Association de la Savonnerie, de la Détergence et des Produits d’Entretien (International Association for Soaps, Detergents and Maintenance Products)

Alkalis
Substances that dissolve in water to yield basic reactions, i.e. they have a pH higher than 7, e.g. sodium hydroxide, soda and sodium silicate

Amphoteric
Amphoteric or ampholytic surfactants are compounds that bear both positively charged ions – cations – and negatively charged ions – anions – and therefore form inner salts that react as an acid or a base depending on the reaction medium

Anaerobic
Conditions characterised by the absence of free oxygen. Mode of life of animal and plant organisms living without free oxygen

Anions
See under ions

Auxiliary industry
Here: industry producing chemicals necessary for the processing of textiles, leather, fur and paper. Surfactants are also used as auxiliaries in a large number of other areas.

Biodegradation
Decomposition of an organic substance (e.g. in water or in soil) through the impact of microorganisms (e.g. bacteria).

Bitumen
Mixtures of high-molecular hydrocarbons derived from crude oil. Used as paints in the roofing felt industry, but mainly as road construction materials

Cations
See under ions

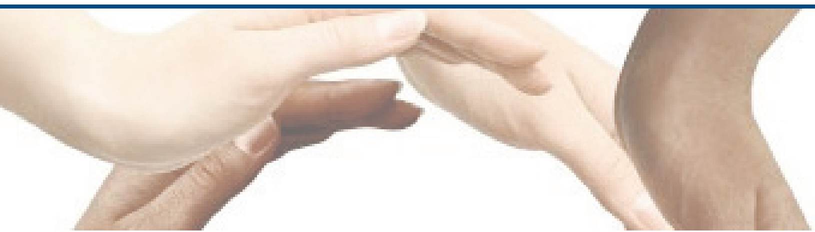
CESIO
Comité Européen des Agents de Surface et leurs Intermédiaires Organiques (European Committee of Organic Surfactants and their Intermediates), an organisation based in Brussels

Coal-water slurries
Suspension of finely ground coal in water

Crude oil demulsifiers
Used to break down an emulsion of water and crude oil. They are highly hydrophilic compounds, e.g. salts of fatty acids and sulphonic acids as well as the acids themselves that are added in small amounts and rapidly break the W/O emulsion.

Deliming agents
They reduce the alkaline swelling required to open the skin during liming and neutralise or remove alkalis and calcium compounds deposited in the hide or skin. Salts, acids and complexing agents are examples of deliming agents.

Detergents
Today: name for washing agents. In the past: name for surface-active agents, i.e. surfactants



Disperse

To spread or distribute one substance as finely as possible in another one

Emulsions, emulsify and emulsifier

Disperse systems of two immiscible or only partially miscible liquids in which one liquid is finely dispersed in the other liquid, e.g. water/oil (W/O) emulsion, i.e. water droplets are distributed or emulsified in an oily phase. Oil may also be emulsified in water resulting in O/W emulsions. Butter is a W/O emulsion and milk an O/W emulsion. Emulsions may be stable for prolonged periods. Their stability is guaranteed for example by surface-active substances, i.e. surfactants, which are called emulsifiers here.

Enhanced oil recovery (tertiary recovery)

Enhanced measures for oil recovery
a) Heat flooding, i.e. heating the oil-bearing rock with hot water or steam (340°C)
b) Solvent flooding, i.e. injecting organic solvents, liquid gases or CO_2
c) Chemical flooding, i.e. injecting surfactants and/or polymer solutions that push the crude oil in front of them

Finish

Finish refers to the finishing treatment of fabrics and textiles, yarns and fibres as well as paper and leather to improve their appearance and/or certain properties. This includes special surface structures, stiffness, softness, gloss, density, smoothness and suppleness as well as water-repellent, flame retardant or anti-microbial finishes.

Flotation

Treatment process for ores, coal and salts (wet flotation process). Ore or coal that is not hydrophilic attaches to froth while wettable gangue sinks down.

Fulling

Felting and thickening (increased shrinkage in length and width) of woollen cloth containing wool or chemical fibres through moisture, heat and pressure

Inhibitor

Substance that prevents or retards a reaction (rusting) or a process (foaming)

Ions

Atoms or groups of atoms with a single charge or multiple charges and positive or negative electric charges. Positively charged ions: cations. Negatively charged ions: anions

Levelness

Uniform attachment, e.g. of a dye

Liming auxiliaries

Chemical products that allow the liming chemicals (mainly sodium sulphite and calcium hydroxide) to penetrate the hide or skin faster and more evenly

Liquor emulsion

Emulsions consisting of fat, water and emulsifiers. In tanning, they are used as fat liquors for conditioning leather after it has been tanned.

OECD

Organisation for Economic Co-operation and Development with 34 member states

Persistent

Continuous, lasting or resisting

Phase-transfer catalysis

Method to bring about or enhance reactions between substances in different phases (e.g. two immiscible liquids). The reaction in the system only starts by adding a small (catalytic) quantity of an agent that transports one of the reactants (most commonly an anion) across the interface into the other phase. Quaternary

ammonium, phosphonium and onium compounds and crown ethers are suitable compounds.

Pickle

Here: to remove oxides (e.g. rust) including metal compounds from surfaces by chemical or electrolytic treatment

Pigment

According to DIN, an inorganic or organic, multi-coloured or neutral colourant that is almost insoluble in the application medium

Polymerisation

Chemical process in which many small molecules of one or several substances (monomers) combine to form large molecules (polymers). The new cluster of molecules has properties different from those of the initial compounds. Plastics are polymers. There are also a large number of other polymers, such as cellulose, starch and protein.

Primary oil recovery

Natural productivity of an oil well (oil is expelled by natural gas or pumped out)

PVC

Polyvinyl chloride. Plastic produced by polymerisation of vinyl chloride

Reviving agents

Textile finishing agents in the form of soaps, oils or fats that prepare chemical fibres for further processing by improving running and slip properties. Reviving agents are designed to give the fabrics (textiles, knitwear, etc.) their specific finishing effect (e.g. suppleness, feel and gloss).

Secondary oil recovery

Increase of the yield of an oil well by injecting natural gas or water However, only about 30% exploitation of an oil field/reservoir is achieved using the methods of primary and secondary extraction. See also enhanced oil recovery

Sizing

Sizing agents give yarns that are intended for weaving smoothness, uniformity, suppleness and strength to improve them for further processing on the loom. They consist either of macromolecular natural products (starch and starch derivatives) or of synthetic polymer products (e.g. polyvinyl alcohol).

Smoothing agent

Sizing additive to improve the softness and smoothness of warp threads

Solubilisation

Surfactant agglomerates, i.e. micelles, are formed in surfactant solutions. Water-insoluble organic substances can be included in the micelles and transferred into the aqueous phase. Although they are not directly in contact with water, they are brought into solution in this way. Solubilising capacity is a characteristic of surfactants.

Surface activity

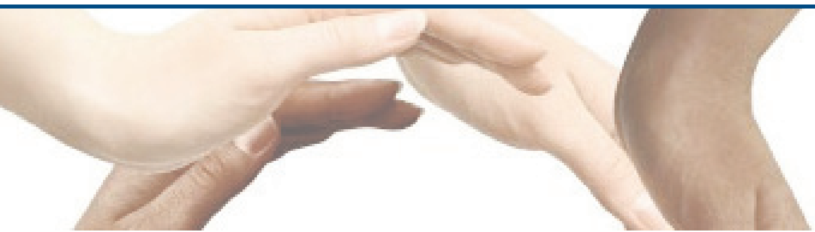
The interface between a liquid and a gaseous phase (water/air) is called surface. Surface-active substances reduce the surface tension.

Suspension

Mixture consisting of small, solid and insoluble particles in a liquid

Wetting agents

Substances that reduce the surface tension of water or other liquids in which they are dissolved, thereby causing them to spread more readily on solid surfaces and, if the surfaces are permeable (e.g. textile fibres), permitting them to penetrate into these surfaces and to wet and soak them thoroughly while displacing the air.



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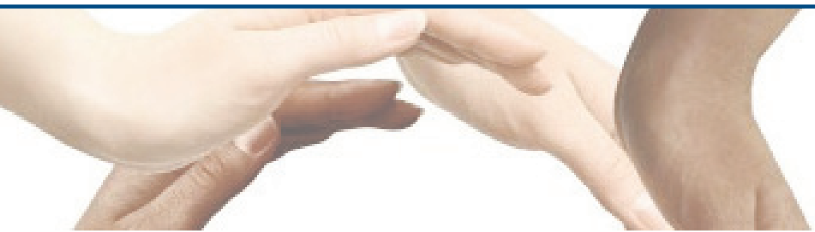

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