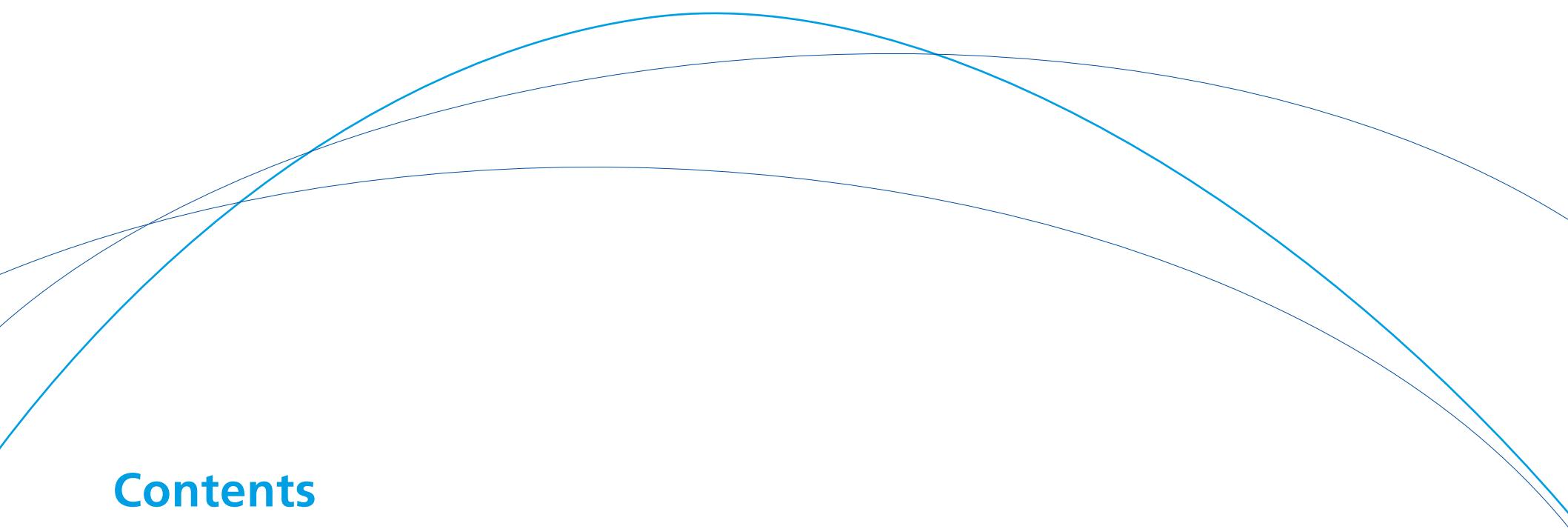




TECHNICAL INFORMATION **ADDITIVES FOR LUBRICANTS**



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Introduction

These days, even the most basic lubricants and metalworking fluids are complex formulations. The applications are becoming increasingly specialized, which means that the requirements on the performance for lubricants and metalworking fluids are becoming ever greater. A lubricant is an optimized combination of base oils and additives, which mutually ensure the most effective performance in the final application.

BYK offers a range of additives that optimize the properties of lubricants and metalworking fluids, thereby ensuring the efficiency can be maximized. BYK additives are not available as "standard packages", but can be individually used. This enables considerable flexibility in the formulation, and a tailor-made customization of the system properties.

The correct additive must be used depending on the application area, in order to optimally adjust the formulation for its intended purpose. This is why BYK first categorizes the additives according to their compatibility/efficiency for the different API classes.

Note

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Various additives are available for each API class. Their mode of action is described in more detail in the following:

- **Defoamers** – act against foam build-up in lubricants or metalworking fluids
- **Wetting and dispersing additives** – disperse solids (oils and aqueous systems)
- **Rheology additives** – prevent solids from settling and adjust the rheology profile (oils and aqueous systems)

The applications for these additives are different as they can range from lubricants such as transmission oils and metalworking fluids to forging lubricants.

API class

I-III	Paraffinic
IV	Polyalphaolefins
V	Naphthenic
V	Esters and others

T.01

Classification of metalworking fluids

Straight/neat oils
Soluble oils
Semi-synthetic
Synthetic

T.02



Defoamers

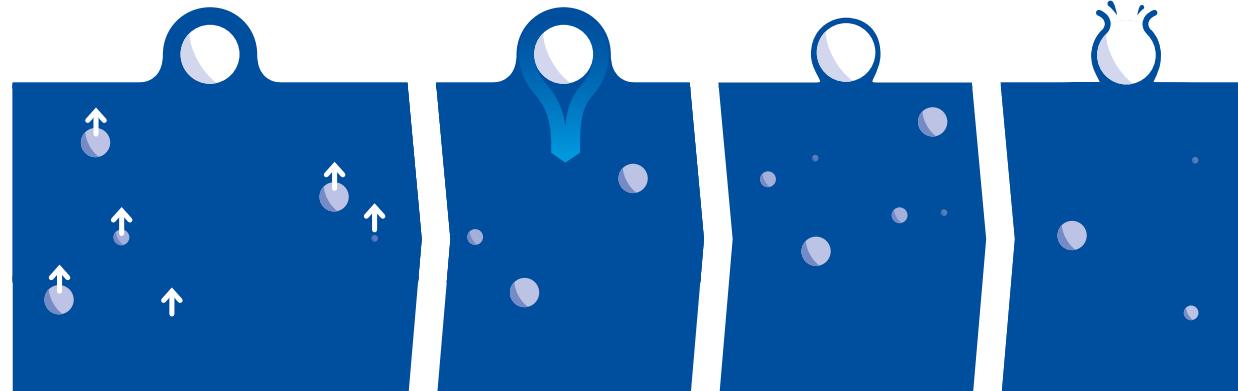
Foam is undesirable in both lubricants and metalworking fluids, as it has a negative influence on lubrication and cooling. This is why defoamers are used here in many cases.

Pure fluids do not suffer from foam build-up, as the gas bubbles rise to the surface as soon as they are produced. Once they reach the surface, the liquid flows downwards out of the foam lamella, i.e. the thin liquid film around the gas bubble. The lamella becomes increasingly thin and the foam bubble bursts (G. 01).

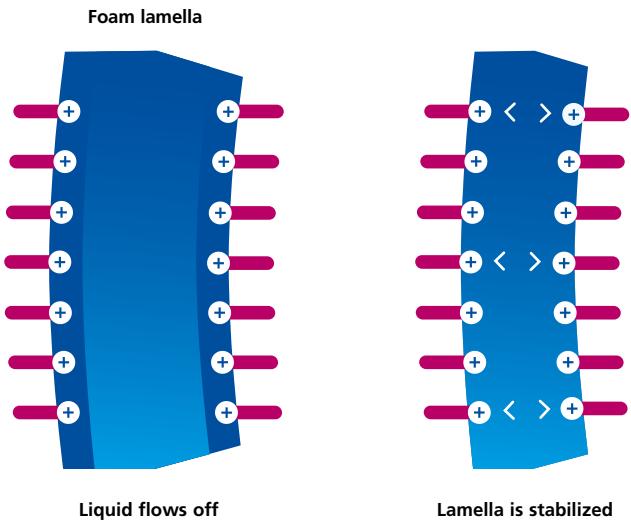
Liquid lubricants and metalworking fluids contain a multitude of additives. The interaction between these additives often creates considerable foam build-up, especially if the lubricants are stirred, pumped or moved in some other way. Additives also ensure that the foam is stabilized and the air cannot escape easily. The reason for this is that many of the additives have a surfactant structure (e.g. emulsifiers). These are surface-active and thereby contain hydrophobic and hydrophilic chemical groups in the molecules.

Due to this structure, they orientate themselves at the liquid/gas interface and stabilize the foam. The foam can only collapse when the liquid escapes from the lamella. If molecules with a surfactant structure are present, they cover the interfaces. The gas bubble migrates upwards and the liquid starts to escape from the lamella. The two surface-laden interfaces of a foam lamella come closer together as liquid drains. When they are close enough, repulsive forces begin to take effect, namely the identically charged repel each other. This causes further drainage of the lamella and break-up of the foam becomes hindered (G. 02).

No foam stabilization in pure liquids



Stabilizing foam



G.01

G.02

Another stabilizing effect results from the Gibbs elasticity of the foam lamella. If you slightly stretch the lamella, this brings about a reduction in the surfactant concentration in the interface, as a greater surface area must be occupied by surfactant molecules, while the quantity of the liquid stays the same. This results in a greater surface tension in this area, as the surfactant concentration is reduced. This greater surface tension pulls the lamella together again, which in turn restabilizes the foam.

Mode of action of defoamers

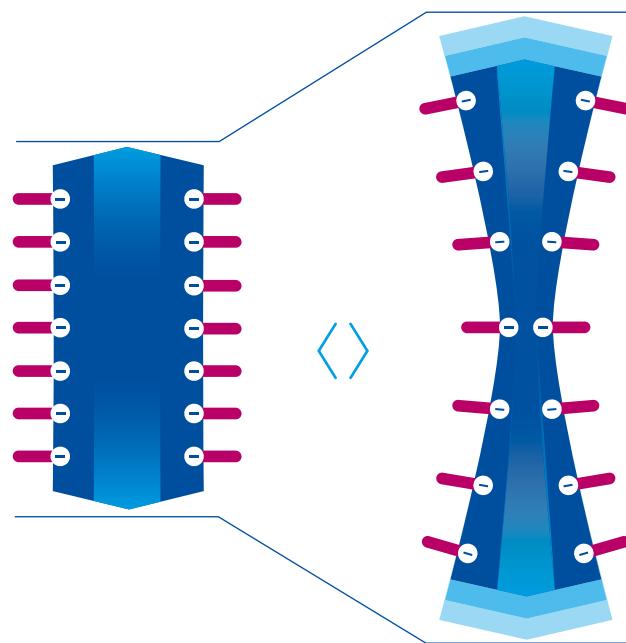
Defoamers are a component in virtually every formulation to efficiently prevent foam build-up.

Defoamers are liquids with low surface tension that need to essentially fulfill three conditions:

- To a certain extent, they must not be miscible with the medium that is to be defoamed
- They need to have a positive entering coefficient, and
- a positive spreading coefficient.

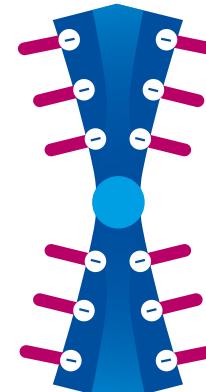
If the entering coefficient is positive, the defoamer can easily penetrate the foam lamella. We consider three different mechanisms when discussing the effect of defoamers: spreading, bridging and absorbing the surfactant molecules by means of hydrophobic components. In each of the mechanisms, the foam-stabilizing surfactant is displaced, and the flexible lamella which is stable against interference, is replaced by a film with lower cohesive forces. The foam lamella can then burst and the foam is destroyed.

The Gibbs-Marangoni effect

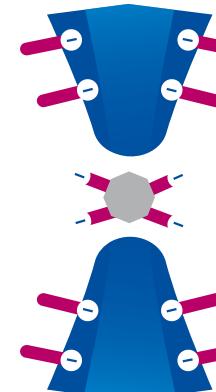


Mode of action of defoamers

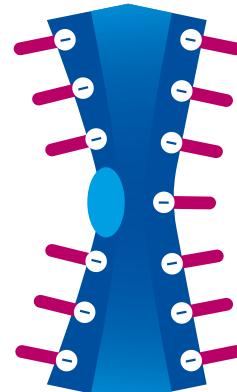
Defoamer destabilizes the lamella (dewetting)



Hydrophobic particles destabilize the lamella



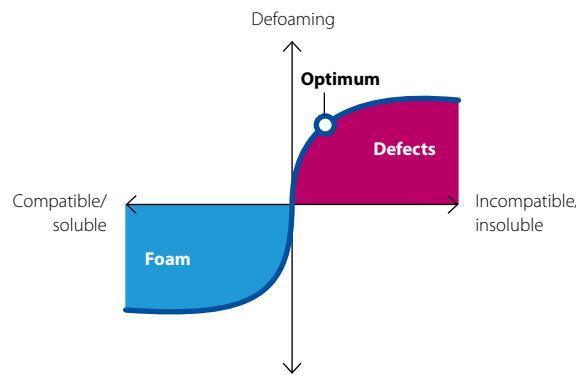
Defoamer destabilizes the lamella (spreading)



Another key feature of all defoamers is their targeted and controlled incompatibility within the medium that is to be defoamed. A compatible defoamer does not migrate directly into the lamella, it is distributed throughout the entire lubricant. The defoaming effect is then only available to a lesser extent or even not at all. With too much incompatibility, the defoamer can create considerable turbidity and could separate after a certain period of storage time. Choosing the correct defoamer is therefore a kind of "balancing act" between compatibility and incompatibility.

Defoamers, which may function very well in some systems, might bring about the formation and stabilization of foam in other lubricants. That's why it is very important to choose the correct defoamer.

Criteria for selecting a defoamer



G.05

Defoamer classes

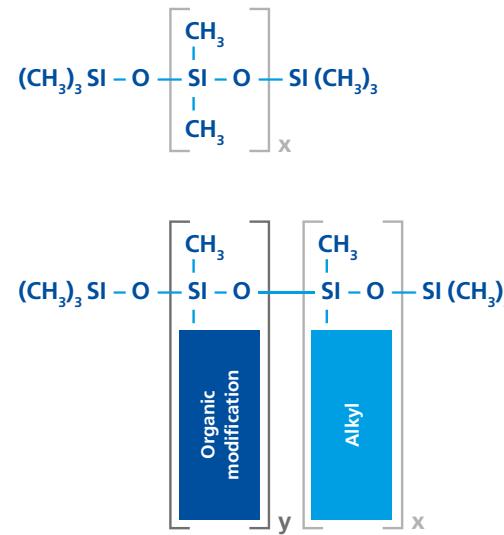
BYK has a broad range of different defoamers which are based on different chemical structures.

The largest class of defoamer is silicone defoamers, which have a particularly low surface tension. The main active substance here is polysiloxane. Of course, these are not simple polysiloxanes, but special organically-modified compounds. The "specific incompatibility" necessary for the silicone defoamers can be achieved in various ways based on the diverse possibilities that silicone chemistry provides. Modifying the silicone backbone with different organic side chains makes it possible to control the compatibility.

It is not only worth considering polysiloxanes as defoamers, there are other polymer compounds that have a defoaming effect as a result of their incompatibility. Finding the right balance between "incompatible" and "compatible" is achieved here by making selective changes to the polarity and molecular weight (molecular weight distribution) of the polymer structures.

When producing lubricants/metalworking fluids, the defoamer is often added at the end of formulation. It is important that it is sufficiently incorporated.

Chemistry of the silicone defoamer



G.06

Testing defoamers

Various test methods are used to test defoamers in lubricants (oils) and metalworking fluids.

The most established method for testing the foam behavior of lubricants/oils is that in accordance with ASTM D 892. In this test, the lubricant is tested at 24 °C and 93.5 °C. The foam is generated in a defined way by aerating the oil through a porous, sintered material made typically from metal or ceramic.

In comparison, metalworking fluids are tested by diluting them in hard or deionized water. A simple shaking test is usually used here in order to establish the amount of foam that can build up.



Wetting and dispersing additives and rheology additives

In the lubricants industry, solid fillers are often added to oils or even water in order to increase the lubricating effect. Examples of these fillers are graphite or molybdenum(IV) sulfide. These solids should be homogeneously incorporated, and in many cases the concentration should be as high as possible. In addition, the solid should settle as little as possible so that it can still be reliably used even after a longer storage period.

Wetting and dispersing additives are used to make sure the solids are homogeneously incorporated. For this purpose, the solids, which in the pure state are often agglomerated,

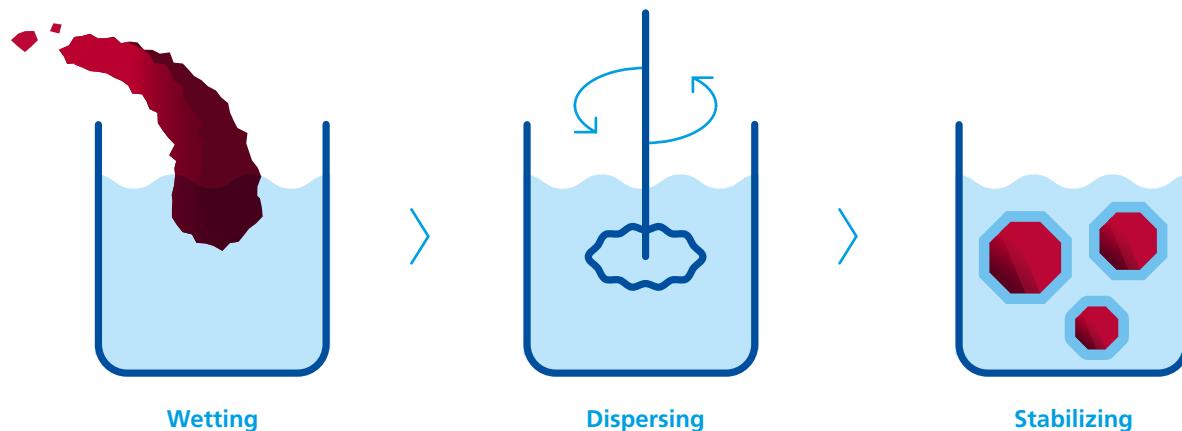
must be distributed homogeneously in a dispersing step. Ideally, they are then available as primary particles.

To achieve this, the solids must be wetted sufficiently with oil or water so that any air and moisture located on the surface can be displaced. In the actual dispersing process, mechanical energy is introduced to the system, which dissipates the agglomerates and ensures a fine distribution. The higher the introduced energy, the better the chances of a good distribution of the filler. Once the filler has been homogeneously incorporated, it should not reagglomerate again if possible. This is prevented by wetting and dispersing

additives. These can stabilize the primary particles in different ways.

Many fillers carry electrostatic surface charges. Using additives, it is possible to strengthen these charges and therefore ensure that all the particles are equally charged. Counterions concentrate in the vicinity of the filler surface in the liquid phase, and this brings about the development of an electrical double layer. This mechanism is used particularly in aqueous systems.

The dispersing process



Dispersing additives which use steric stabilization, are characterized by a special structure. They contain one or more groups that have an affinity to the filler. These anchor or adhesive groups are responsible for a strong and permanent absorption on the surface of the filler. The second characteristic is the chains that are compatible with the lubricant/water, which, after the absorption of the additive on the filler surface, protrude as far as possible and extend into the surrounding lubricant/water. This forms a layer around the filler, which means that the filler particles cannot come into direct contact with one another and therefore are effectively prevented from reagglomerating.

A combination of the two modes of action (electrosteric) is also possible.

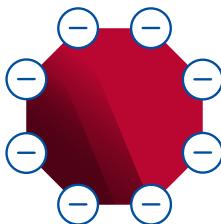
It is important that both the wetting and the dispersing additives as well as the fillers are incorporated well. The wetting and dispersing additives should be incorporated first at high shear rates, and then the filler can be added. This should also be incorporated at high shear rates. The dosage of the wetting and dispersing additive is made by % based upon solids.

The good distribution of the filler particles generally ensures a reduction in the viscosity of the solution. In many cases, this enables an increase of the solid content in the lubricant. Many fillers have the tendency to settle and form a sediment. This is undesirable in the application and especially when storing the product. The settling can be reduced by changing the flow behavior of the solution.

Some wetting and dispersing additives are effective, however rheology additives are generally still used to optimally adjust the properties.

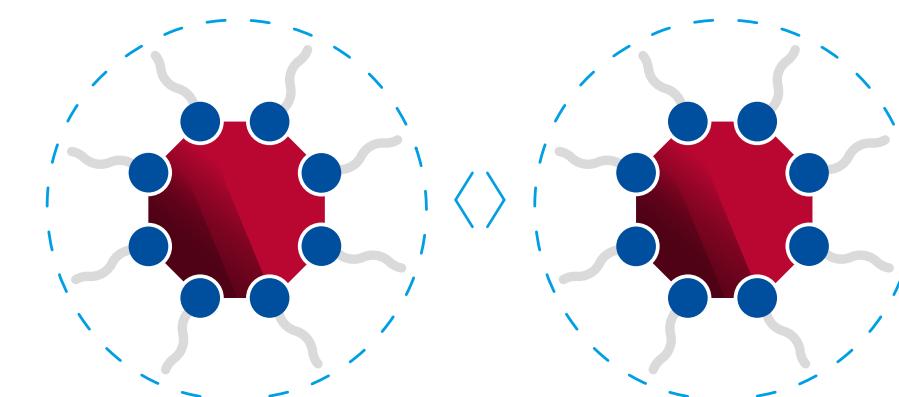
There are a multitude of additives on the market which specifically influence rheology. Generally speaking, the mechanism is always the same: in the liquid phase, the additives develop spatially extended three-dimensional network structures which reversibly collapse under shear.

Different stabilization mechanisms for wetting and dispersing additives



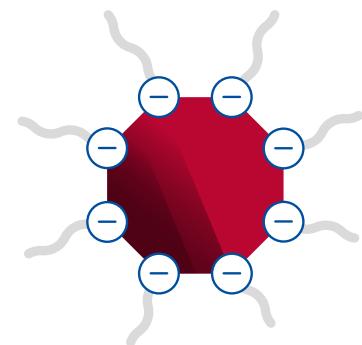
Electrostatic stabilization

- Mainly in aqueous systems
- Sensitive to
 - Ion concentration
 - Changes to the pH value



Steric stabilization

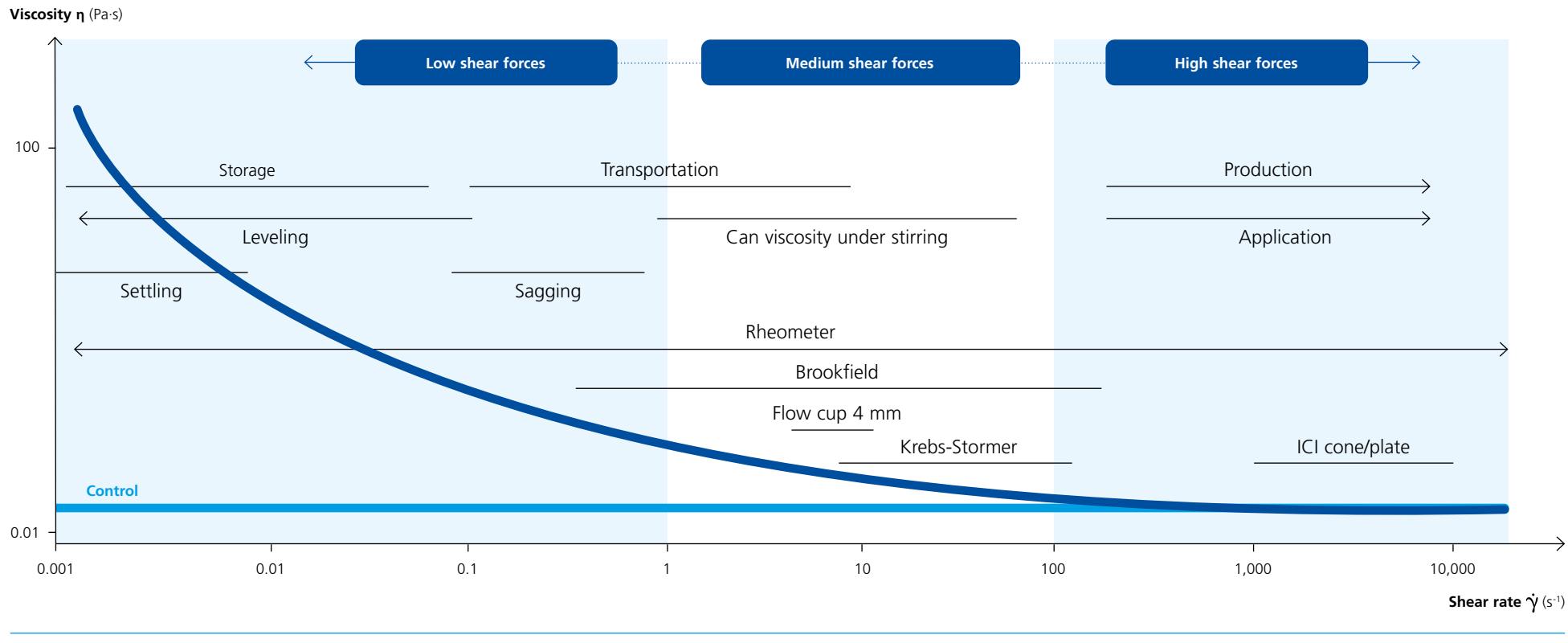
- For aqueous and solvent-borne lubricants



Electrosteric stabilization

- Combination of electrostatic and steric stabilization

Shear rates of typical applications/procedures



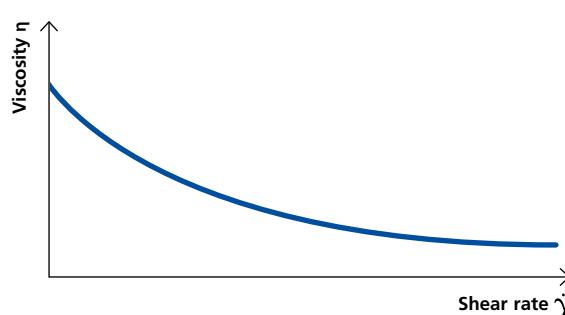
Depending on the additive and the concentration used, it is possible to create a rheology profile that is optimum for the final product. The important thing is to specifically define this profile. G.09 shows the shear rate ranges for different industrial process steps.

Overview of the viscosity profiles

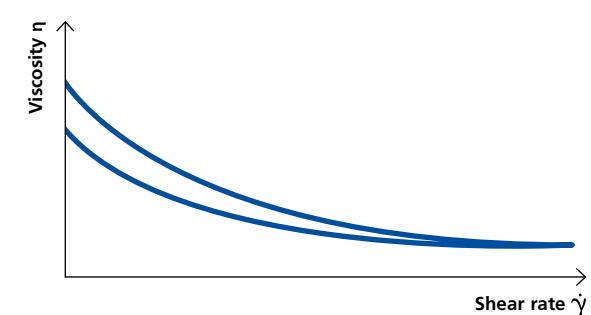
Newtonian flow behavior



Pseudoplastic flow behavior



Thixotropic flow behavior



The storage of the product takes place at very low shear rates. Here, the viscosity should generally be very high in order to prevent the filler from settling. In the application itself, the viscosity should be lower to enable the product to be applied.

To achieve this, usually a thixotropic or pseudoplastic flow behavior is set. This flow behavior is characterized by a high viscosity when the product is stored, and a considerable reduction in the viscosity as soon as shear energy is introduced to the solution. Once the shear stress is removed, the network of the additives is formed again, and the viscosity increases.

Structure of the network of clay minerals



G.11

This behavior can be generated by different groups of additives, for example clay minerals. These are powdered and, depending on the modification, can be incorporated into aqueous or organic solvents/oils. The clay minerals are made up of particles in which many silicate platelets are stacked on top of each other.

These have to be separated from each other, and then form a network in which they coordinate over hydrogen bonds. It is important that these are added to the system under high shear to enable optimum dispersal of the platelets. In organic systems/oils, an activator must be used in the majority of cases to separate the platelets from each other as effectively as possible and to support the formation of the network. The clay minerals usually have a thixotropic flow behavior.

Another possibility is liquid rheology additives which are available for aqueous and solvent-borne systems/oils. The liquid additives usually generate thixotropic or pseudoplastic flow behavior. These additives are polymers which form a network under lower shear stresses, which is then destroyed at high shear rates. The process is reversible. As soon as the shear is removed, the network is rebuilt.

An example here is a polyurea thickener, which coordinates using a network of hydrogen bonds. Depending on the modification of the molecules, these are either compatible with water or solvents/oils.

Structure and network formation of polyurea additives

Chemical structures

RHEOBYK-410



RHEOBYK-411

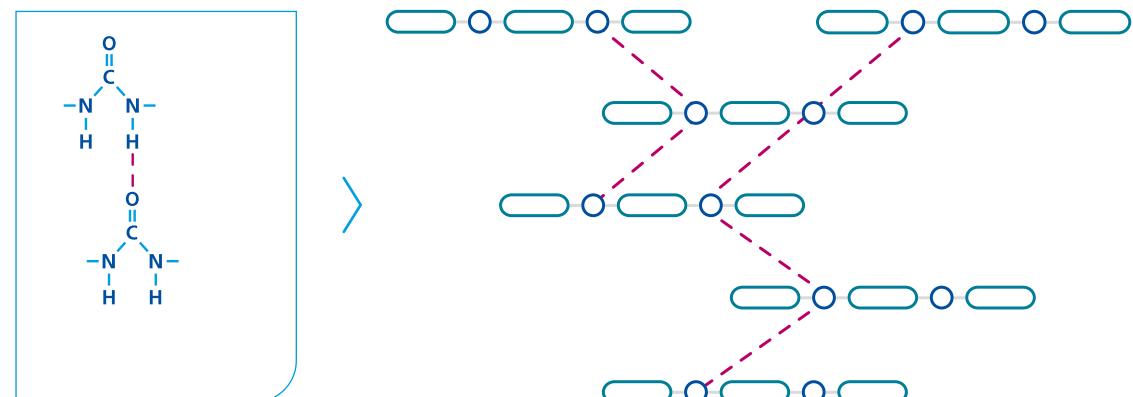
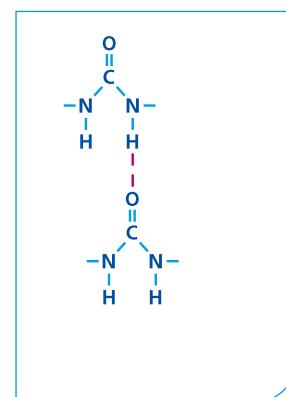


RHEOBYK-420



● Urea groups Modifying groups: ● high polar ● medium polar ● low polarity

Structure formation via hydrogen bonds

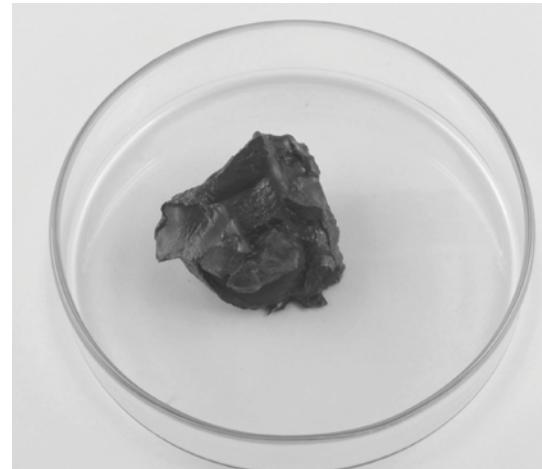


The advantage of liquid additives is that they are easier to incorporate, and can often be post-added. Nevertheless, the incorporation should take place at higher shear rates to enable homogeneous distribution.

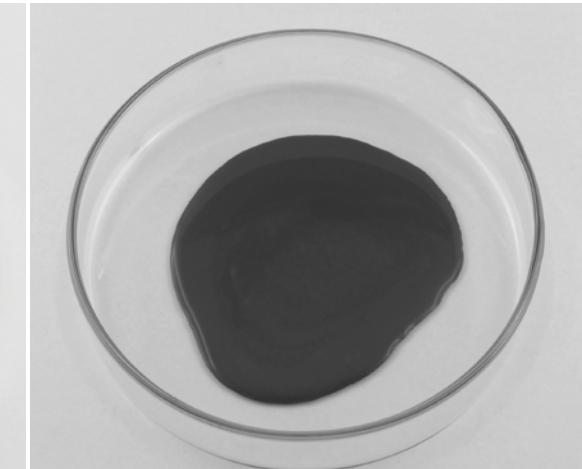
At the beginning of additive selection, you must be sure of the requirements and the possibilities of the flow behavior of the final product. If, for example, you require anti-settling behavior, the viscosity should be as high as possible at low shear rates. Here, a strong network is formed, which stabilizes the particles in the solution. The type of application (e.g. spraying, pumping, rolling) defines the viscosity that is possible in the higher shear ranges. In most cases, these requirements result in thixotropic flow behavior for the application.

Examples of the successful application of wetting and dispersing additives and rheology additives are forging lubricants. These are highly filled systems, often with graphite, which must be storage stable and nevertheless easy to apply. G. 13 shows an example in water with and without additives.

Effect of wetting and dispersing additives in combination with rheology additives



30 % graphite in water
without additives



40 % graphite in water with wetting and
dispersing additive and rheology additive

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