Whitepaper

Polyurea-based rheology control agents efficiently stabilize oil-based dispersions

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Abstract

BYK-GO 8730, a new liquid and easy-to-handle additive, facilitates control of the rheological behavior in low-polarity liquids such as mineral and synthetic oils. The rheology additive effectively prevents the sedimentation of particles such as guar gum, xanthan gum, or friction reducers in these oils. Storage-stable suspensions of these particles can now be prepared, transported, and used on site. Easy incorporation and fast processing are benefits compared to established technologies.

BYK-GO 8730 key benefits

- Easy to use; no shear or heat activation necessary
- Provides a "particle-free" system
- Works with many types of polymer powders (polyacrylamide, guar gum, cellulose, etc.)
- Liquid handling form, suitable for cold weather with pour point below -17 °F/-27 °C
- Works in all typical base oils (BTEX-free mineral oils, diesel, and others)

Settling issue in oil-based dispersions

In the various stages of gas and oil production (drilling, cementing, stimulation, production), a wide range of oil-based particle dispersions (sometimes also referred to as slurries) are employed.

For example, solid powdered thickeners for aqueous systems such as guar gum or xanthan gum are dispersed in non-polar liquids, e. g. refined mineral oils, diesel fuel, or synthetic paraffins and olefins, to provide a liquid delivery form which allows for easy handling on site. Such slurries are used to thicken processing fluids as their incorporation into these aqueous systems is much easier compared to direct incorporation of the solid powdered thickeners.

Another example are dispersions of friction reducers as they are commonly used in aqueous systems to establish laminar flow under high shear conditions due to high pumping rates.

To facilitate the handling of dry powdered friction reducers, the particles are pre-dispersed in a non-polar liquid as described above, and the resulting oil-based slurries are added on site into the water stream pumped into the formation.

Without the addition of a rheological additive (also referred to as anti-settling additive), the dispersed particles suspended in the oils are subject to sedimentation. Traditionally, organoclays or styrene/olefin block copolymers are utilized as rheological additives to prevent this. However, in some applications, inorganic particulate additives such as organoclays are undesired due to unfavorable interactions with the formation.[1,2] The production of dispersions stabilized by styrene/olefin block copolymers can be time and energy consuming and, therefore, disadvantageous.

Working mechanism of rheological additives

There are in principle two ways of preventing settling of particles in dispersions:

1. Increasing the viscosity of the liquid phase
2. Increasing the elastic properties of the liquid phase

In the first case, the viscosity of the liquid phase is so greatly increased by a rheological additive that the particles do not settle any more or the settling time is greatly prolonged. This mode of action has the disadvantage that the high viscosity of the dispersion strongly impairs its further handling (pumping, mixing, etc.). Moreover, syneresis due to gravity is only prolonged in this case, but finally inevitable despite the elevated viscosity.

In the second case, the viscosity of the dispersion is not altered by the rheology additive. The additive increases the elastic properties of the liquid phase, also referred to as the induction of a yield point, which effectively prevents the dispersed particles from settling.

Liquid urea thixotropes as easy-to-handle rheology control agents

Rheology control agents based on urea chemistry represent a class of liquid and easy-to-handle additives which can be used to control the flow behavior of liquid formulations and provide, among other benefits, efficient anti-settling properties.[3] These additives can provide thixotropic flow behavior to liquid compositions over a relatively wide polarity range from waterborne formulations up to paint and resin systems of comparatively low polarity.[4] The general chemical structure and functional groups providing the rheological effect can be seen in Fig. 1; however, established products fail to provide sufficient rheology control in non-polar hydrocarbon systems as typically used in gas and oilfield operations.

Typical structure of a urea-based rheology additive

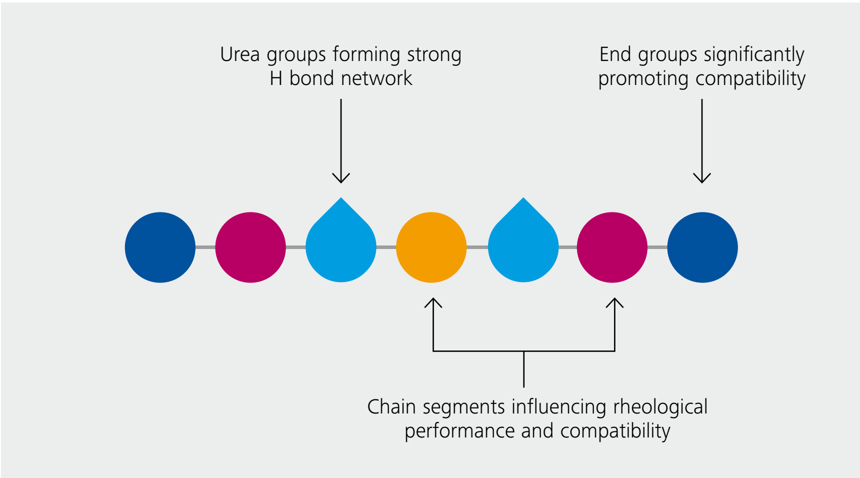
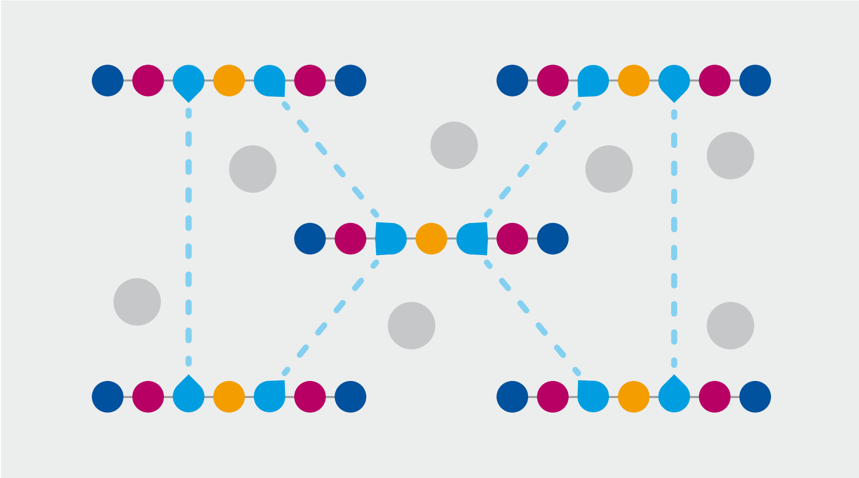


figure 1

BYK-GO 8730: superior network stabilization via yield point

To overcome the aforementioned challenge, a rheology control agent with low impact on viscosity but providing sufficient elastic properties to achieve a yield point would be desirable. This typically is a strength of urea-based liquid thixotropes in polar to medium or less polar systems. The general mechanism of network formation involves a formation of hydrogen bonds via the urea groups, therefore generating a three-dimensional reversible network (cf. Fig. 2). Once the network is formed, the liquid is equipped with increased elastic properties, thus preventing particles in the fluid from settling. To this end, the nature of the particle (for example organic or inorganic) or the particle surface (for example acidic, basic, or neutral) is not of significance with exception of the particle density and size.

Network formation and particle stabilization using liquid thixotropes



Urea groups forming strong H bond network
Chain segments influencing rheological performance and compatibility
End groups significantly promoting compatibility
Particle

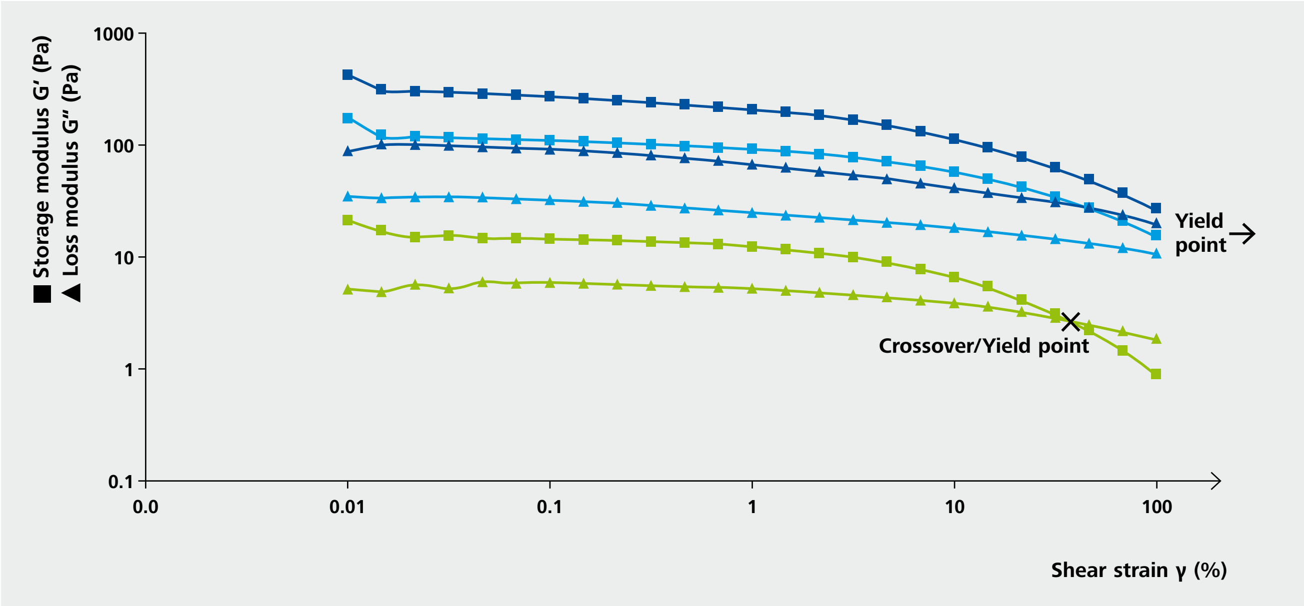
figure 2

To meet the requirements for rheology control of non-polar systems like hydrocarbons, structural adjustments of the additive chemistry were necessary. The main task here is to provide an additive solution which shows good storage stability of the liquid additive itself, sufficient compatibility in the final formulation, as well as sufficiently low solubility to promote the molecular interaction of the thickener molecules with each other in the application system.

The three-dimensional network formed by BYK-GO 8730 modifies the viscoelastic properties of the material. Viscoelastic properties are the sum of the viscous properties, which can experimentally be determined as loss modulus G", on the one side and elastic properties, measured as storage modulus G', on the other side. Viscous properties describe the energy that is applied to a system upon deformation and "lost" due to dissipative processes. On the other hand, elastic properties describe the energy which is stored in the system upon deformation and which can be recovered afterwards (comparable to elongation of a spring). Viscoelastic properties can be investigated using a rheometer oscillation measurement. In contrast to a rotational test which is commonly used to determine a viscosity value, the weak interactions determining the viscoelastic properties require a non-destructive oscillation test. In this experiment, the frequency of the oscillation and the amplitude (strain or force) can be varied. Eventually, the ratio between viscous and elastic properties can be characterized, and information about the strength of the structure (yield point) can be obtained.

Oscillation measurement results shown in Fig. 3 underline this effect: The addition of the new urea-based rheology additive BYK-GO 8730 to an oil-based slurry not only increases the general level of storage modulus G' and loss modulus G", but also furthermore shifts the crossover point to higher shear strain values, i.e. the structural stability is maintained even at elevated deformation.

Storage (■) and loss modulus (▲) as function of the shear strain in a BTEX free mineral oil guar slurry with and without BYK-GO 8730



- 0.75 % active substance BYK-GO 8730
- 0.50 % active substance BYK-GO 8730
- Without additive

figure 3

Use as anti-settling additive for organic thickener powders and friction reducers

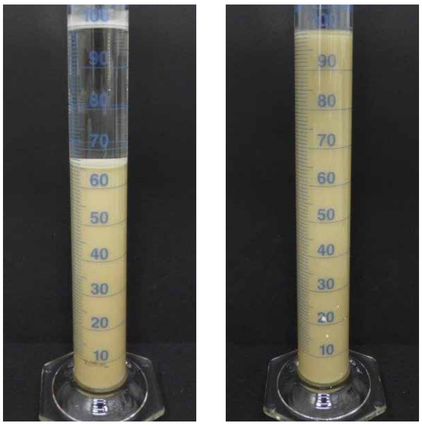
The oil and gas industry employs various types of polymer powders like guar gum, xanthan gum, or polyacrylamides to increase viscosity in water-based systems. Adding the powder directly into water creates the danger of lumps, agglomerates, and less efficient viscosity increase and, to avoid these drawbacks, the polymer particles are pre-dispersed into an oil to create a slurry with typically 50 % particles and 50 % oil. Without adding anything else, these particle-in-oil slurries will quickly sediment and form a hard settlement. Therefore, to ensure a stable and safe handling of these slurries, there is the need to adjust the rheology by optimizing the anti-settling properties.

The new polyurea-based rheology control additive has been developed as an easy-to-use anti-settling additive, especially for the typical carrier oils like BTEX-free mineral oils or diesel. The additive features a liquid delivery form and only needs to be added under mixing conditions. In comparison to organoclays, there is no need for an activation process; in contrast to styrenic block copolymers, it does not require any kind of temperature activation.

For oilfield applications like guar slurries or friction reducer slurries, a typical dosage of the BYK-GO 8730 is between 1 and 2 % delivery form on total. The additive can be added under mixing conditions into the base oil, and the powder is added afterwards and then mixed until homogeneous. Incorporation of BYK-GO 8730 under higher shear energy allows for improved handling and optimum performance.

Another advantage of BYK-GO 8730 for oilfield application is the organic polymeric nature of the rheology additive. There are no inorganic particles involved which always have the danger of blocking pores in the formation. This makes it very useful for all stimulation applications where this requirement is highly appreciated.

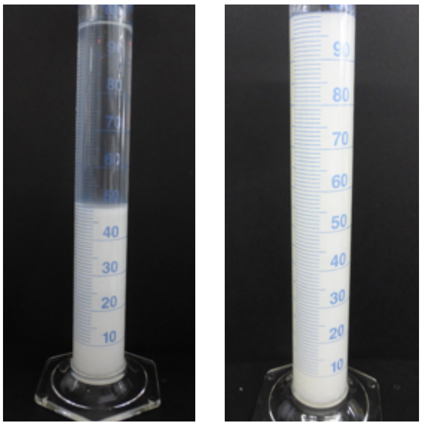
Example of a guar gum in oil slurry



Left picture: phase separation in the absence of an additive; right picture: stabilized system in the presence of the new polyurea-based rheology additive BYK-GO 8730

figure 4

Example of a friction reducer in oil slurry



Left picture: phase separation in the absence of an additive; right picture: stabilized system in the presence of the new polyurea-based rheology additive BYK-GO 8730

figure 5

Summary

A new liquid and easy-to-handle polyurea-based rheology additive can provide a sufficient yield point to effectively prevent sedimentation without severely impacting the viscosity profile of liquid oil formulations. While applications of this effect are manifold, one example is the improved storage stability obtained with slurries of solid rheology control agents for aqueous systems (e.g., guar gum) or friction reducers in low polarity oils, which can be prepared, transported, and finally used on site without sedimentation issues. Compared to existing solutions, BYK-GO 8730 does not require a special activation process and is a particle-free liquid.

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