

RHEOLATE[®] alkali swellable emulsions

Technology and chemistry of ASE and HASE based rheology modifiers for aqueous systems



Key Benefits

- ❖ Highly effective
- ❖ Improved application properties
- ❖ Potential liquid alternatives for cellulosics, e.g. HEC
- ❖ Resistant to microbiological and enzyme spoilage

Introduction

HASE and ASE based rheology modifiers are belonging to polymeric thickeners and find use in the formulation of aqueous systems, such as paint and coatings, adhesives, construction materials etc.

The flow characteristics and properties are, depending on the product, are very similar those provided by cellulose ether, e.g. hydroxy ethyl cellulose (HEC)

Both terms, ASE and HASE, are abbreviations for the following:

The terms ASE abbreviates **A**lkali **S**wellable **E**mulsion and indicates traditional, unmodified thickeners. On the other hand, HASE means **H**ydrophobic mod. **A**lkali **S**wellable **E**mulsion and has been used for thickeners which are combining the characteristics of ASE with an additional partial associative mechanism.

Both ASE and HASE have been based on a vinyl copolymer chemistry. In case of the modified HASE grades, the mentioned associative functionality has been implemented by additional hydrophobic parts into the thickener molecule.

All products are provided as APEO and VOC free flowable liquids with an active content of 25% to 30%. However, also a 100% active, powdered version is available.

All alkali swellable thickeners are versatile and can be used combined with all other classes of rheology modifiers.

Key properties

- ◆ Easy to use
- ◆ Improved spattering resistance
- ◆ Superb application properties
- ◆ Quick viscosity recovery for good sag control
- ◆ Ease of addition/post addition possible
- ◆ Increased processing speed
- ◆ Resistant to microbiological and enzyme attack
- ◆ Balanced flow and sag properties
- ◆ Thixotropic flow characteristics

Mechanism

Both types of alkali swellable emulsions, HASE and ASE, have been based on vinyl copolymer chemistry. The polymer itself is water insoluble and consists of additional polyacrylic acid parts. These are causing the acidic conditions of the product in the delivery form (pH 3 - 5).

In the delivery form, the rheologically active polymers has been present as tight, coiled chains. Raising the pH to approximately 7, initiates the dissociation of the acid groups. This results in a beginning uncoiling process of the coiled chains driven by magnetic repulsion due to the negative charges at the neutralized carboxylic groups. This process has been visualized in *Figure 1*.

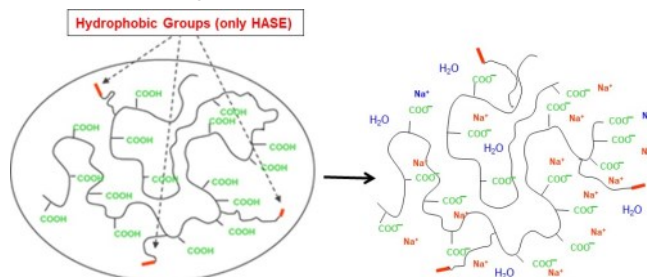


Figure 1: Neutralization ASE/HASE

On complete dissociation (pH ~9) the chains reach their maximum extension and develop viscosity in the system by macromolecular extension.

Hydrophobically modified HASE products, have additional, less polar groups attached along their backbone (in *Figure 1* marked in red). These hydrophobic side groups also interact or associate with each other and with other formulation components. This dual thickening mechanism is very important for the performance of the additive in the final formulation.

Alkali swellable emulsions are thickening highly effective. They are enzyme resistant and can be used as a partial or full replacement for e.g. Cellulosics in various formulations. All ASE and HASE products provide thixotropic flow connected with a high low shear viscosity values. As a results, alkali swellable emulsion typically give excellent suspension and sag control. They also offer ease of hndling and the flexibility of post addition.



The rheological behaviour is typically controlled by the molecular weight of the thickeners active component, the exact monomer composition as well as the type and the degree of the hydrophobic modification.

As visualized in Figure 2, traditional ASE grades tend to give the most shear thinning flow. These grades are typically used for e.g. for spray applied industrial coatings.

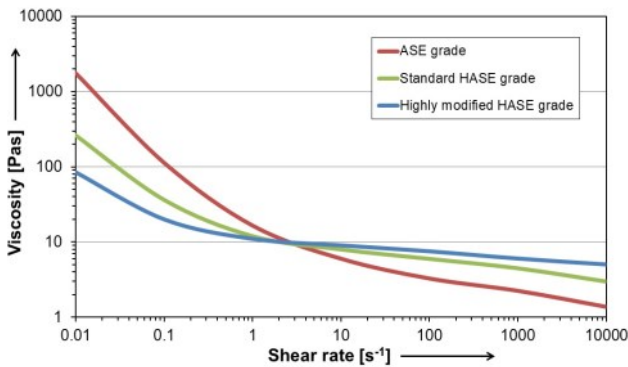


Figure 2: ASE/HASE influence on flow characteristics

The polymer chains take a little time to reorient when shear is removed so structural recovery is not instantaneous. Thus, the system formulated with this thickeners is thixotropic which leads improved levelling and optimized application properties.

The hydrophobically modified HASE thickeners dual or hybrid mechanism of action makes them excellently suitable for decorative coatings. The associative thickening mechanism takes longer to reorient and equilibrate. A much higher degree of thixotropy is the result. These products are also easier to handle as they react more gently to changes in the systems pH.

The hydrophobic components makes the polymers more volume filling which causes higher viscosities under the influence of shear. This typically leads to a better brush drag and film build. Roller spattering is significantly reduced due to the improvement of the viscoelastic characteristics. These effects are becoming stronger with increasing amount of hydrophobic modification in the thickeners molecule.

As the molecules swell under alkaline conditions, it is clear that the pH of the system needs to be controlled. As shown in Figure 3, the optimum performance can be obtained in a pH range of 8 - 10.

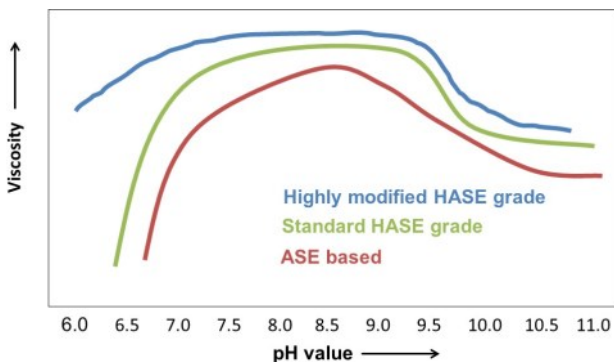


Figure 3: ASE&HASE ph dependency

A correction is required for both, viscosity stability and batch-to-batch reproducibility. Some of the additives are less sensitive to pH variations than other. This is a consequence of the polymer chemistry. Typically highly modified HASE grades are providing stable viscosity over the widest range of pH. This is a result of the high amount of hydrophobic modification as the associative mechanism remains unaffected from pH variations. With decreasing amount of associative acting groups in the molecule, the applicable range of pH is shrinking. As a consequence, unmodified ASE thickeners are providing their maximum performance only over the most narrow range of pH.

However, for both thickener classes it is relevant that leaving the optimum range of pH is resulting in viscosity losses. At too low pH, the incomplete neutralization resulting in improperly uncoiled molecule chains is the result. A too high pH causes so called „salting out“ effects of the rheologically active molecules by the excessive supply of cations.

In general, it is recommended to use a stable, organic pH buffer such as amino alcohol rather than e.g. ammonia. This will avoid issues with pH drift on storage due to volatilization.



However, further factors are having an influence on the efficiency of alkaline swellable emulsions.

Coalescing agents chemistry tend to have little influence on the performance. Nevertheless, it is very important for the hydrophobically modified grades.

In general, the more polar or water miscible the coalescent, the more it will reduce the viscosity developed at low or mid shear rates (Figure 4).

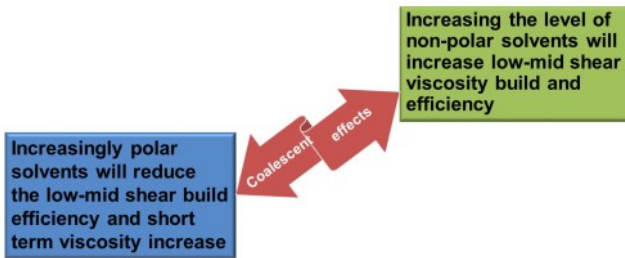


Figure 4: Coalescent influence on HASE efficiency

On the other hand, less polar or less water miscible coalescent are enhancing the the associative effect and cause a rise of the low shear viscosity. This behaviour can be used to fine tune the final systems performance such as sag control, levelling performance, etc.

However, also the composition of the surfactant package of a system has a large influence on the thickening efficiency and the stability (Figure 5).

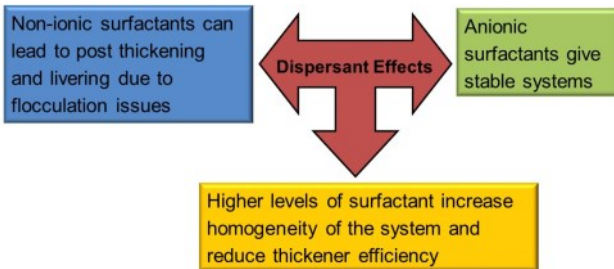


Figure 5: Surfactants influence on HASE efficiency

The most stable formulations can be achieved with standard anionic surfactants. With some non-ionic grades, post-thickening or even livering might occur over storage time. An explanation for this effect is that, because the alkali swellable polymer carries slightly negative charges, it might displace the nonionic surfactant from whichever surface it is protecting. The long chain thickener polymer can than bridge the particles and allow flocculation or at least a significant viscosity increase. Experience has shown that the use of organic buffers as neutralizing aid can help to reduce this issue if it occurs. In general, post-thickening is more common with unmodified ASE grades than with HASE products but much more

depends on the full formulation and strength of the associative interactions.

Alkali swellable emulsions are water thin and, in the majority of the cases, be post-added directly utilizing moderate shear. Under certain circumstances, e.g. small binder particle size, low or zero VOC, or larger pH differences between the thickener and the system, rapid, localized gellation might occur. This can result in the formation of isolated gel particles or seeds. In very extreme cases the entire system might shock resulting in an unworkable mass. If occurring, this effect can be prevented simply by diluting the additive with water (and/or if coalescents e.g. glycols are appropriate):

Alkali swellable emulsion	1 Part
Water and/or coalescent	1 Part
Mix until uniform, than add slowly to the system	

This is generally recommended when only low shear mixing is available or in cases were hydrophobic modified alkali swellables are used with very fine particle size binders.

Alkali swellable rheology modifiers can be used to provide a more thixotropic millbase assuming the appropriate pH can be achieved. In this case, only a part of the proposed additive content (about one third) should be used. The remaining portion should than be added to the letdown as usual.

As the hydrophobically modified grades thicken by a dual mechanism, they will take time for full equilibration. It is important to allow this during the initial formulation. Approximately 80% of the full viscosity is developed within the first 2 hours after manufacturing. The rest builds with 24 hours. This effect is totally reproducible and be acommodated in quality control testing. Non hydrophobically modified thickeners equilibrate much more quickly due to their simpler thickening mechanism.

An overview on the available alkali swellable RHEOLATE® products and their proposed uses can be found below.

RHEOLATE® 1 ASE	RHEOLATE® 125 ASE	RHEOLATE® 185 HASE	RHEOLATE® 150 HASE	RHEOLATE® 175 HASE	RHEOLATE® 425 HASE	RHEOLATE® 465 HASE
Shear thinning	Very shear thinning	Low shear rate range	Low to mid shear rate range	Mid to high shear rate range	Low to mid shear rate range	Mid to high shear rate range
<ul style="list-style-type: none"> Low PVC decorative systems and putty systems 	<ul style="list-style-type: none"> Industrial coatings and construction systems 	<ul style="list-style-type: none"> Mid to high PVC paints 	<ul style="list-style-type: none"> Mid to high PVC paints 	<ul style="list-style-type: none"> Mid to high PVC paints 	<ul style="list-style-type: none"> Mid to high PVC paints 	<ul style="list-style-type: none"> Mid to high PVC paints
<ul style="list-style-type: none"> Alternative grade to cellulosics Gentle structure build Easy to handle Sag stability Storage stability 	<ul style="list-style-type: none"> Provided optimum sprayability Rapid viscosity recovery Excellent sag control Circulation stability 	<ul style="list-style-type: none"> Econ. alternative to HEC Prevents hard sedimentation Excellent hiding power Superb roller spattering and levelling Less mud cracking 	<ul style="list-style-type: none"> Balanced flow and levelling To replace cellulose ether 	<ul style="list-style-type: none"> Excellent film build Good levelling Excellent spatter resistance 	<ul style="list-style-type: none"> Balanced flow and levelling Good allrounder Improved spatter resistance Balance of sag and levelling 	<ul style="list-style-type: none"> Provides alkyd like flow and levelling Excellent brush drag and improved hiding power Superiour spattering resistance
30% active	25% active	30% active	30% active	30% active	30% active	30% active

NOTE: The information herein is currently believed to be accurate. We do not guarantee its accuracy. Purchasers shall not rely on statements herein when purchasing any products. Purchasers should make their own investigations to determine if such products are suitable for a particular use. The products discussed are sold without warranty, express or implied, including a warranty of merchantability and fitness for use. Purchasers will be subject to a separate agreement which will not incorporate this document.

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