

Contact worldwide

Asia
BASF East Asia Regional Headquarters Ltd.
45/F, Jardine House
No. 1 Connaught Place
Central
Hong Kong
formulation-additives-asia@basf.com

Europe
BASF SE
Formulation Additives
67056 Ludwigshafen
Germany
formulation-additives-europe@basf.com

North America
BASF Corporation
11501 Steele Creek Road
Charlotte, NC 28273
USA
formulation-additives-nafta@basf.com

South America
BASF S.A.
Av. Faria Lima 3600 – 10º andar
Itaim Bibi – São Paulo – SP
04538-132
Brazil
formulation-additives-south-america@basf.com

BASF SE
Formulation Additives
Dispersions & Pigments Division
67056 Ludwigshafen
Germany
www.basf.com/formulation-additives

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Practical Guide to Rheology Modifiers



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Formulation Additives by BASF


The Chemical Company

We create chemistry

FOREWORD

BASF

is the world's leading chemical company and a premiere provider of innovative solutions for the paints and coatings industry. BASF offers virtually every ingredient needed to make high quality coatings, along with the know-how to solve formulation challenges and support the development of new coating concepts. The portfolio encompasses polymer dispersions, pigments, resins and a broad range of additives such as light stabilizers, photoinitiators and formulation additives.

We combine our understanding, listening and collaboration skills in order to best serve the needs of our customers. With global manufacturing capabilities, a strong research and development platform, full-service regional technical laboratories, pre-screening capabilities and a team of knowledgeable, experienced experts, BASF can help to make your coatings better and your business more successful.

When it comes to formulation additives, BASF has a strong portfolio of industry-leading products that help to enable sustainable and performance-driven solutions. Our offer comprises the broadest technology base of dispersing agents, wetting & surface modifiers, defoamers, film forming agents and rheology modifiers..

Rheological additives are key ingredients in paints, coatings and inks as they help control the coating application and the final appearance. BASF offers six classes of rheological additives for paints and coatings: -

- Alkali swellable emulsions (ASE)
- Hydrophobically modified alkali swellable emulsions (HASE)
- Hydrophobically modified polyurethanes (HEUR)
- Hydrophobically modified polyethers (HMPE)
- Attapulgites (inorganic rheology modifiers)
- Castor oil based thixotropes

Each product class has its own characteristic properties. Understanding the background of the technologies and functions of each additive class is essential when formulating a modern paint or coating system. BASF develops and offers innovative solutions, from basic compounds to final formulations, ensuring the perfect interaction of binder and thickener. Production process efficiency is key, endeavoring to optimize our customers' manufacturing operations and render them more cost-effective with our rheological additives. Harmony between product development and production process is a prerequisite for end products to score high in the market place.

This booklet has been developed in order to give first-hand guidance on the use of rheological additives from BASF and to make the most out of their performance characteristics.

Looking for innovative solutions where little helpers make all the difference for your high quality coatings?

BASF – The Chemical Company



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Rheology Modifiers: An Introduction

Rheological additives

are key ingredients in paints, coatings and inks as they control the precise properties and characteristics of fluid products. Without these special additives, such media would be as "runny" as water. During application, paints would spatter in all directions, have little hiding power and exhibit a much shorter shelf life. Rheology modifiers enable formulators to adjust the flow behavior of paints and coatings. That way, painters benefit from improved viscosity and application characteristics.



Rheology modifiers from BASF reduce dripping and spattering of paint during roller or brush application. Sag resistance of paint is improved by a rapid but controlled viscosity increase after application. During transport and storage of the paint, the rheology modifiers prevent sedimentation of the pigments within a formulation. Rheology modifiers ensure that the end product achieves the desired balance between consistency, durability and good application properties.

Especially in water-based paints, the high interdependency of the individual coating raw materials like binders, surfactants or pigments requires a lot of experience and expertise to achieve the ideal rheological profile. BASF engineers and technologists offer precisely the experience and scientific competence required to meet the toughest demands of today's technical challenges and environmental regulations.



Rheology Background

Rheology Background

Terms & Definitions

Rheology (Greek: rheos = flow or streaming) is the study of deformation and flow of substances. When force is applied to a liquid, the liquid will flow to relieve the strain from this force. Different systems will resist this flow more than others and the measurement of this resistance is a measure of the viscosity of the system. Isaac Newton first introduced a basic model for the flow measurement of a liquid between two parallel plates (fig. 1):

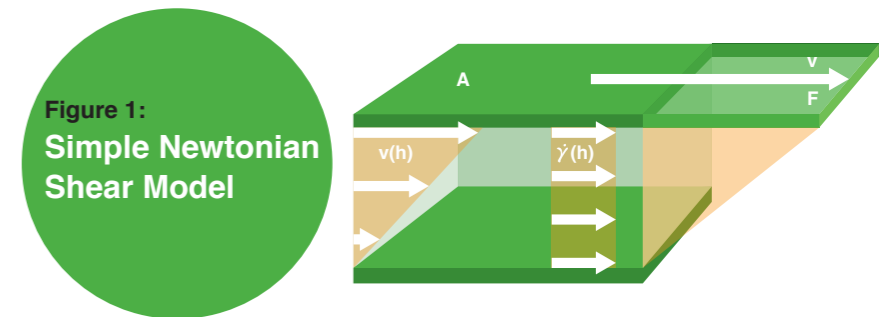


Figure 1:
Simple Newtonian
Shear Model

Imagine a fluid located between a static plate and another plate moving at a certain velocity. The viscosity, the most frequently used rheological parameter, is calculated from the shear rate $\dot{\gamma}$ and the shear stress τ according to the following equation:

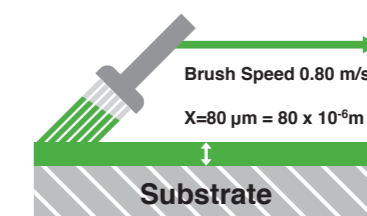
$$\eta [Pa \cdot s] = \frac{\tau [Pa]}{\dot{\gamma} [s^{-1}]}$$

Shear stress τ is the force (F) applied to the rectangular surface (A) when this is deformed by shear strain.

The **shear rate** of a fluid flowing between two parallel plates, one moving at a constant speed and the other one stationary is defined by the velocity v and the distance h .

$$\dot{\gamma} [s^{-1}] = \frac{v [m \cdot s^{-1}]}{h [m]}$$

The shear rate applied during the application of a coating can vary from several hundred up to thousands of reciprocal seconds depending on the application method used. An impressive example is the shear rate generated during simple brush application (fig. 2):



$$\text{Shear rate} = 0.8/80 \times 10^{-6} = 1 \times 10^4 \text{ s}^{-1} = \underline{10.000 \text{ s}^{-1}} !$$

Figure 2: Simple brush application of a paint system already results in a shear rate of about 10.000 s^{-1}

▪ Rheology:

(Greek: rheos = flow or streaming)
Study of deformation and flow of substances

▪ Viscosity:

Frictional forces in a system and thus the resistance in a liquid to flow

▪ Newtonian flow:

Viscosity of a substance is constant at different shear rates

▪ Pseudoplastic flow (shear thinning):

Viscosity decreases with increasing shear rate

▪ Thixotropic liquids:

Liquids that show a time dependent rebuild of viscosity after shear force is removed

▪ Dilatant liquids (shear thickening):

Liquids that show viscosity increase with increasing shear rate

Rheology Background

Rheology Profiles

If the viscosity of a substance is constant at different shear rates, it is said to exhibit ideal or "Newtonian viscosity" (Fig. 3). Newtonian flow is generally found only with low-molecular weight liquids such as water, solvents and mineral oils.

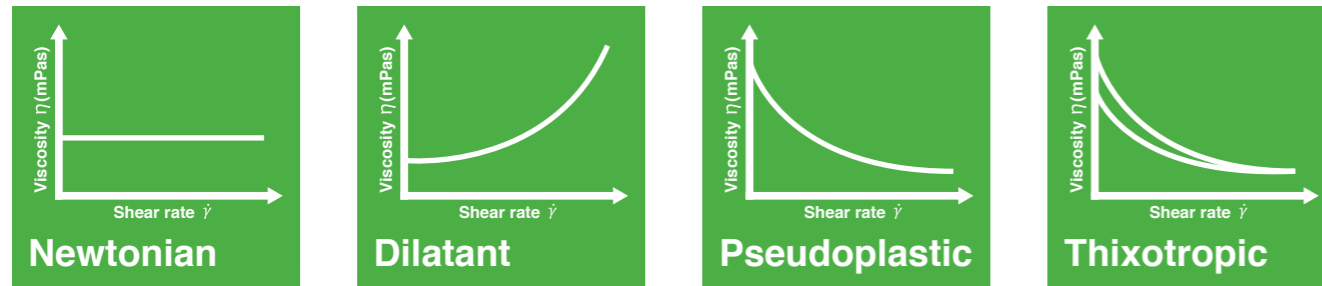


Figure 3: Overview of different shear profiles

In practice, more complex systems have flow properties which depend on the shear rate. If the viscosity decreases with increasing shear rate, the flow behavior is said to be shear thinning or pseudoplastic. Most coatings and polymer solutions show a pseudoplastic behavior.

Thixotropic liquids show a time dependent rebuild of viscosity after shear force is applied. Once the shearing force is stopped the viscosity recovers with time. The degree of thixotropy is generally represented by the so called hysteresis area. Thixotropic behavior is beneficial in paints applied to vertical surfaces, where the viscosity reduces under the shear of the brush or roller, allows flow and leveling and then recovers to prevent sagging.

Materials whose viscosity increases with increasing shear rate are dilatant (shear thickening). Dilatant behavior is shown by, for example, binder systems with high solids content or high polymer concentrations. Dilatant behavior is usually undesirable in industrial practice and can lead to problems with processes involving pumping or stirring.

The whole life cycle of a paint or coating (e.g. manufacturing, stirring, filling, storage, application, brushing, spraying) can be associated with different shear rates and rheological demands (Fig. 4).

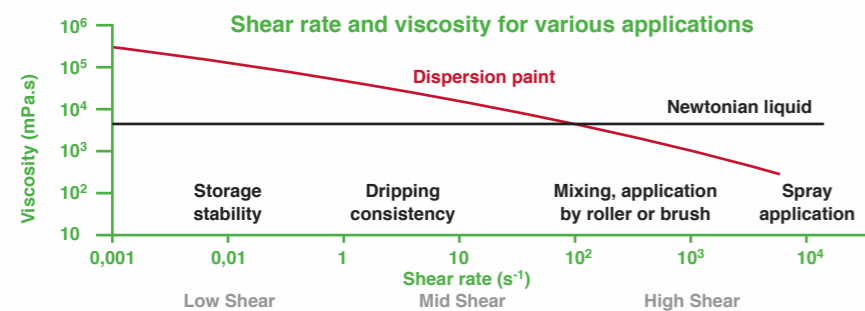


Figure 4: Different shear rates and applications associated therewith

Viscosity, in particular non-Newtonian viscous behavior, is an important material property that contributes to a fluid's performance. Because paints are rendered pseudoplastic, they show high stability during storage. Settling is avoided due to the supporting higher viscosity at low shear (gravity) conditions. A relatively high viscosity at low shear rates means also that higher amounts of paint can be held on a brush without dripping. Pumping and general mixing of ingredients are carried out at low to medium shear rates. Application of the paint or coating generally happens under relatively high shear conditions (brushing, spraying). Here a lower viscosity is beneficial (Fig. 5).

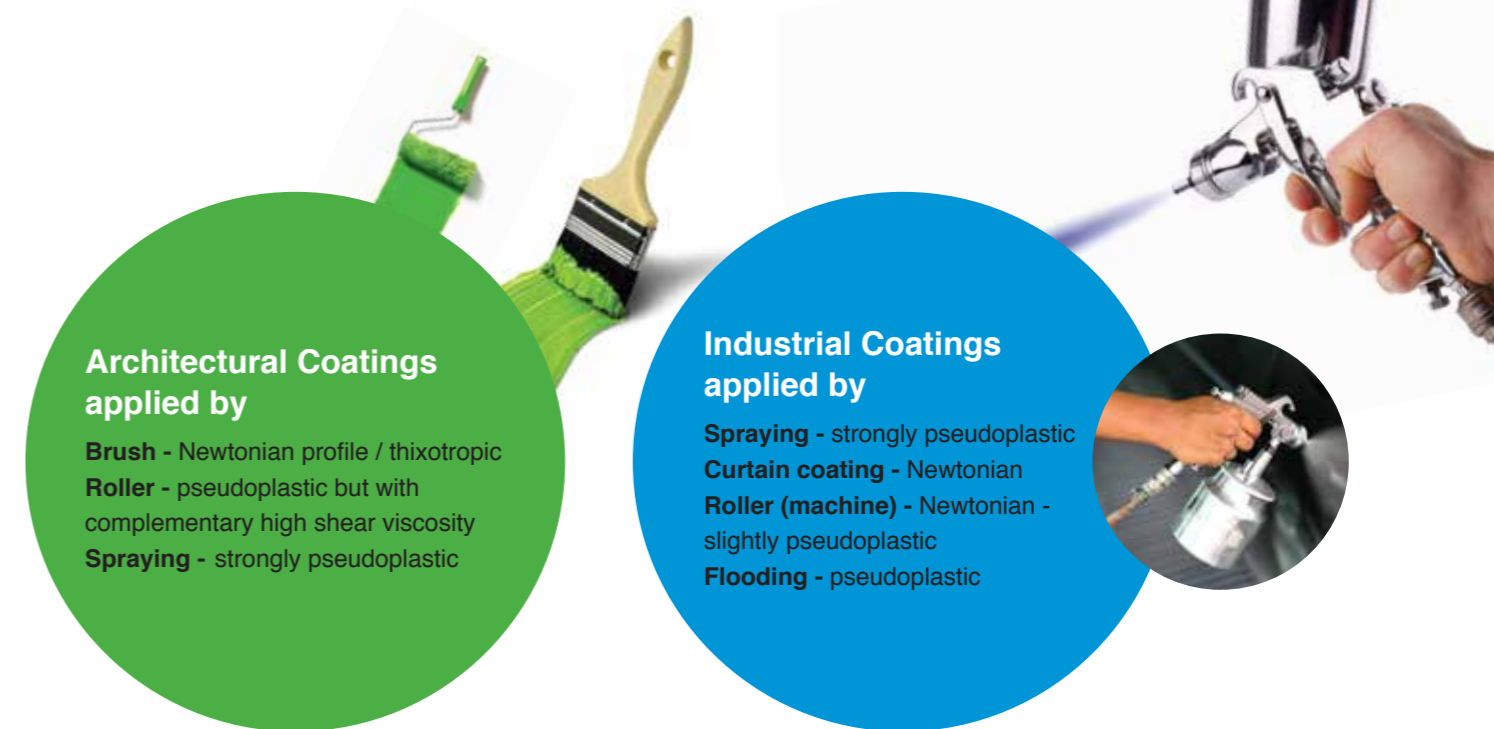


Figure 5: Application techniques and corresponding desired rheology profiles

Paints often require a degree of leveling after application, so it may not be desirable to have too fast recovery of viscosity. However, too slow recovery can lead to sagging and dripping. Other systems may require more instantaneous recovery of viscosity. In such cases a good knowledge of the flow behavior imparted by different rheological additives will aid selection of the best products for the desired application.

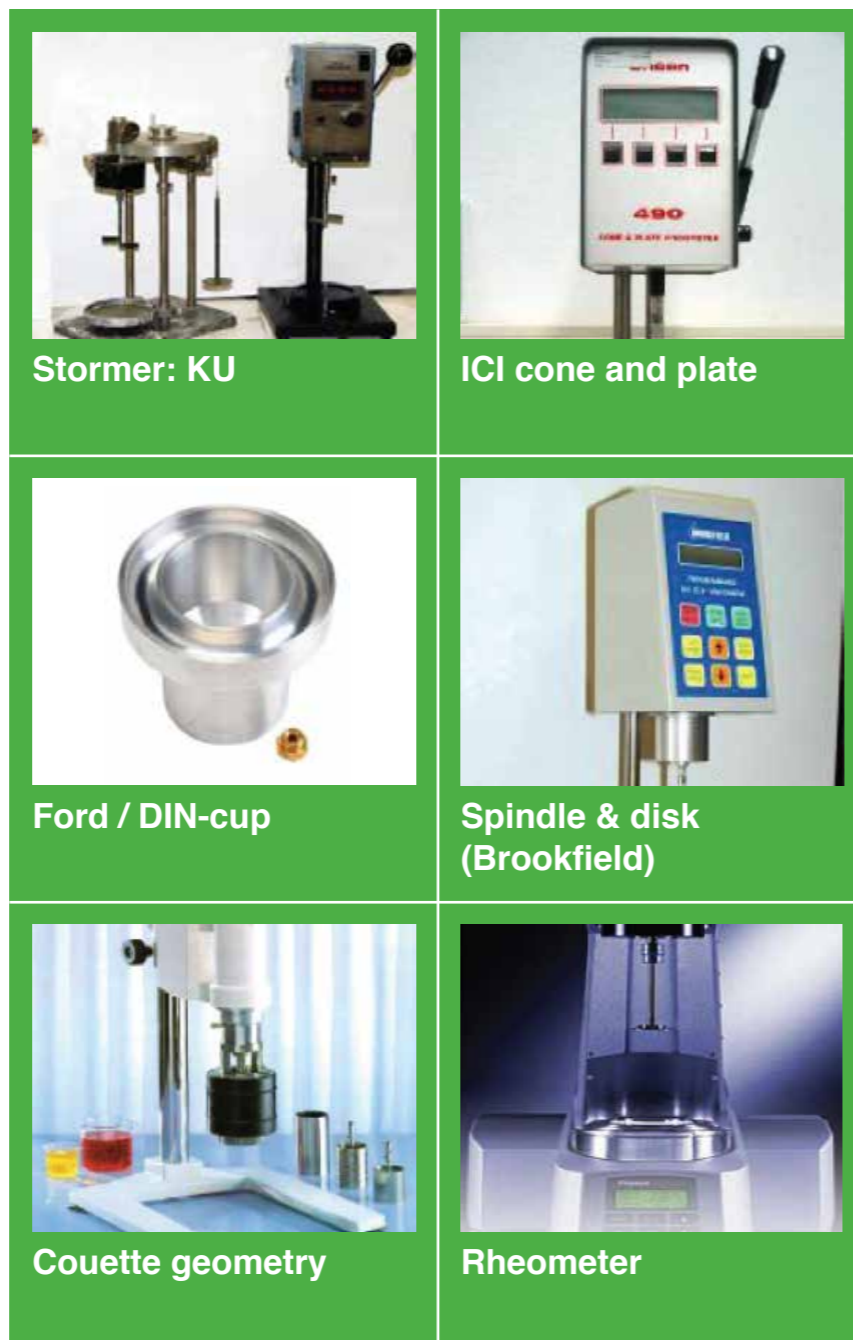
With rheology modifiers from BASF, it is possible to create a wide variety of rheological profiles. The behavior of your products can easily be rendered either more Newtonian (brush, roll-on, curtain coating) or more pseudoplastic (sprayable coating) in nature to ensure optimized application properties.

Rheology Background

Techniques to Measure Rheological Effects

- **Brookfield viscometer:**
Covers low to medium shear range
- **Krebs Stormer viscometer (KU):**
Covers medium shear range
- **ICI Cone and Plate viscometer (ICI):**
Covers high shear range
- **Rheometer:**
Universal, low to high shear range

Formulators use a number of viscometer types and methods to measure and understand the behavior of their formulations. Some common viscometer types are listed in Figure 6 together with the shear rate ranges they typically represent.



Brookfield and Krebs Stormer viscometers are common tools which are simple to operate and are often used as quality control tools to measure the viscosity at a given temperature and specific shear conditions.

A Brookfield viscometer measures the torque required to rotate a spindle in a fluid. For a given viscosity, the viscous drag, or resistance to flow (indicated by the degree to which the spring winds up), is proportional to the spindle's speed of rotation and is related to the spindle's size and shape. By changing speeds and spindles, a variety of viscosity ranges can be measured.

For a more complete understanding of the rheology profile of your system it may be necessary to use a rheometer that can make multiple measurements over a wide shear range. Precise measurement of low, medium and high shear rate viscosities can be made with more advanced rheometers. Such a rheometer can work in various modes (e.g. controlled shear stress mode, controlled shear rate mode or oscillatory mode). Through continuous or ramped measurement such an instrument follows the change of flow parameters and accurately measures shear rates, shear stress and viscosities over a wide range of conditions.

It is also worth mentioning that various flow cup types exist and are used as QC tools to check viscosities in a quick and easy way. The flow time is related to the viscosity of the liquid.



Figure 6: Various devices to measure viscosity

Chemistry of Rheology Modifiers

- **Inorganic rheology modifiers:**
are based on inorganic products like clays or silicas
- **Organic rheology modifiers:**
are based on organic products like cellulosics, polyacrylates or polyurethanes
- **Associative rheology modifiers:**
thickening by non-specific interactions of hydrophobic end-groups of a thickener molecule both with themselves and with components of the coating ("physical network")
- **Non-associative rheology modifiers:**
thickening by an entanglement of water-soluble, high molecular weight polymer chains



Chemistry of Rheology Modifiers

Rheology Modifiers are organic or inorganic coating additives that control the rheological characteristics of the liquid formulation. In coatings technology, rheology modifiers are mainly used to provide either pseudoplastic or thixotropic properties.

Their rheological properties are determined by the composition and concentration of their ingredients in the coating formulation consisting of binders (polymers, oligomers, reactive diluents), solvents (organic, aqueous), pigments (organic, inorganic), and fillers and additives (stabilizers, initiators, catalysts, etc.). Thus, there are no universal solutions for all coatings but many different technologies and products with more or less clear application limits. In addition, the required rheology profile for a coating formulation may vary dramatically during its lifetime, starting from the manufacturing process, through transportation and storage, and finally during (industrial) application processes.

Today, we know numerous technologies to influence the rheology profile of paints and coatings. All available rheology modifiers can be divided into inorganic and organic chemistries (Fig. 7).

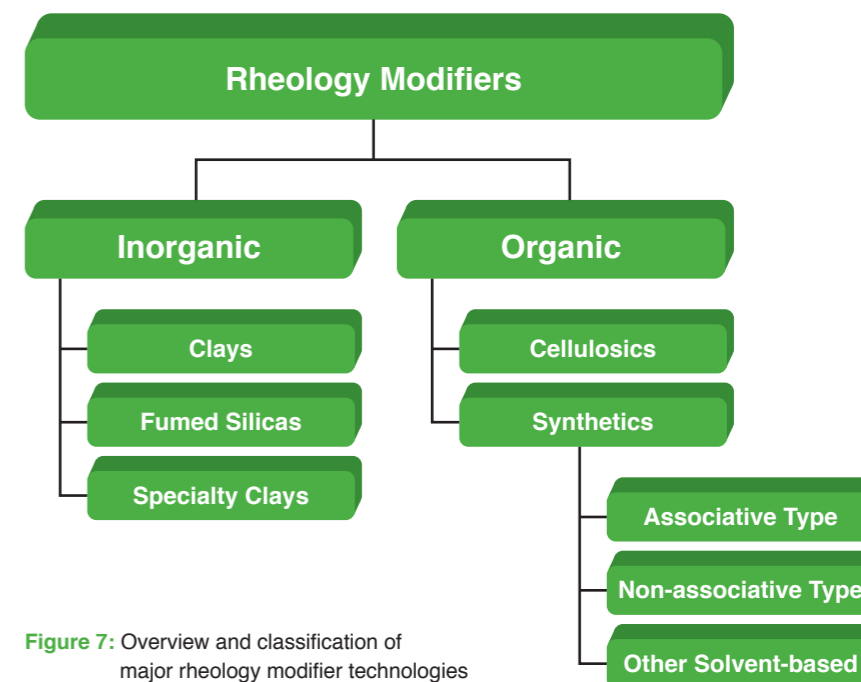


Figure 7: Overview and classification of major rheology modifier technologies

Inorganic Rheology Modifiers

The most common types of modified and unmodified inorganic rheology modifiers are attapulgite clays, bentonite clays, organoclays, and treated and untreated synthetic silicas. Most inorganic thickeners and rheology modifiers are supplied as powders. If they are properly dispersed into a coating, they usually function as suspending or gelling agents and some have secondary use as extenders for pigments. Inorganic rheology modifiers tend to have high yield values and are characterized as thixotropes.

Usually the viscosity of the formulation decreases with time under constant shear conditions as its gel structure is broken down. If the shear is removed, the coating gradually recovers to its original viscosity. Certain grades or mineral types are useful for thickening aqueous systems and others for solvent-based coatings. Utility in one media or the other is mostly a function of the thickener's particle surface, which can be organically modified to render it hydrophobic for solvent-based coatings.

Inorganic rheology modifiers are sometimes added to aqueous formulations as secondary thickeners to improve the anti-sag, anti-settling, anti-syneresis and anti-spattering properties of a coating.

Organic Rheology Modifiers

Organic rheology modifiers are more diverse than inorganic ones. They can be subdivided into products based on natural raw materials, like cellulose or xanthan, and products based on synthetic organic chemistry, like polyacrylates or polyurethanes. Again, the synthetic products can be subdivided into associative and non-associative rheology modifiers: -

Non-associative rheology modifiers

These act via entanglements of soluble, high molecular weight polymer chains ("hydrodynamic thickening"). The effectiveness of a non-associative thickener is mainly controlled by the molecular weight of the polymer. Formulations thickened non-associatively have pseudoplastic rheology with highly elastic properties. This produces good stabilization against settling and low sagging with even high-build coatings. Non-associatively thickened systems often exhibit limited flowability. The high molecular weight of the polymers can sometimes lead to compatibility problems such as flocculation.

Associative rheology modifiers

These thicken by non-specific interactions of hydrophobic end-groups of a thickener molecule both with themselves and with components of the coating. They form a so called "physical network" (Fig. 8).

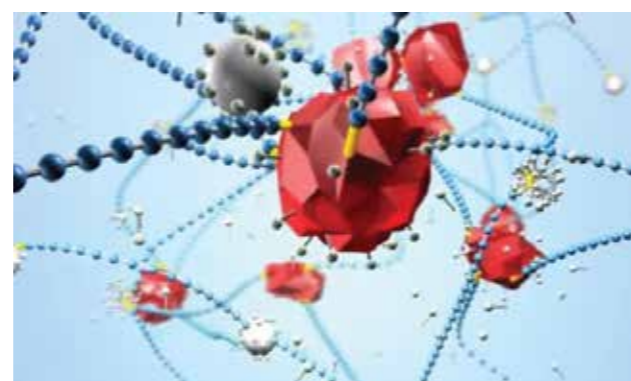


Figure 8: Formation of a physical network

In contrast to non-associative types, associative thickeners interact with the polymer dispersions used as the binder. The hydrophobic terminal and side groups of these thickeners combine to form networks that serve to increase viscosity.

Rheology Modifiers for Water-based and Solvent-based Systems

All thickener technologies can also be divided into thickeners for aqueous and non-aqueous (solvent-based) formulations. Common thickener technologies for solvent-based paints and coatings are organoclays, hydrogenated castor oils, fumed silicas or polyamides. Thickeners for water-based systems include cellulosics, acrylic thickeners (ASE/HASE), associative thickeners (HEUR, HMPE) as well as specialty clays. Figure 9 gives an overview of the main advantages and limitations of each technology.

Water-based media:

Product	Advantages	Limitations
Cellulosics	Wide range of applications Shear thinning for easy application Colorant compatibility Open time control by water retention Sag control	Flow and leveling Roller spattering Effect on water and scrub resistance Negative influence on gloss Easy biodegradation
Acrylics (ASE, HASE)	Strong shear thinning Anti-settling and anti-sag Cost advantage Good spray properties	pH sensitivity Effect on water and scrub resistance
Associative (HEUR/HPME)	Excellent flow and leveling Low shear thinning Minimized roller spattering Gloss High film build	Viscosity-loss-on-tinting Sag control
Specialty clays	Sag resistance Heat resistance	Incorporation Flow and leveling Open time control

Solvent-based media:

Product	Advantages	Limitations
Organoclays	Wide range of applications Shear thinning for easy application Thixotropic flow with excellent sag resistance Heat resistance	Incorporation, shear required Not generally suitable for clear coats Reduced gloss, poorer leveling Less thixotropy than organics
Hydrogenated castor oil	Excellent thixotropic flow Strong shear thinning Leveling Sag resistance	Temperature control Requires adequate shear and dwell time Cool down before packing (false-body) Seeding Solvent dependency
Polyamides	No max temperature Excellent thixotropy Strong shear thinning Quick film build Universal	Minimum processing temperature Requires adequate shear and dwell time Intercoat adhesion
Fumed silicas	Chemically inert Heat resistance	Shear sensitivity Difficult to disperse

Figure 9: Common rheology modifier types for aqueous and non-aqueous formulations

BASF's Rheology Modifiers Product Range

BASF Formulation Additives offer six classes of rheological additives for paints and coatings (Fig. 10): -

- Alkali swellable emulsions (ASE)
- Hydrophobically modified alkali swellable emulsions (HASE)
- Hydrophobically modified polyurethanes (HEUR)
- Hydrophobically modified polyethers (HMPE)
- Attapulgites (inorganic rheology modifiers)
- Castor oil based thixotropes

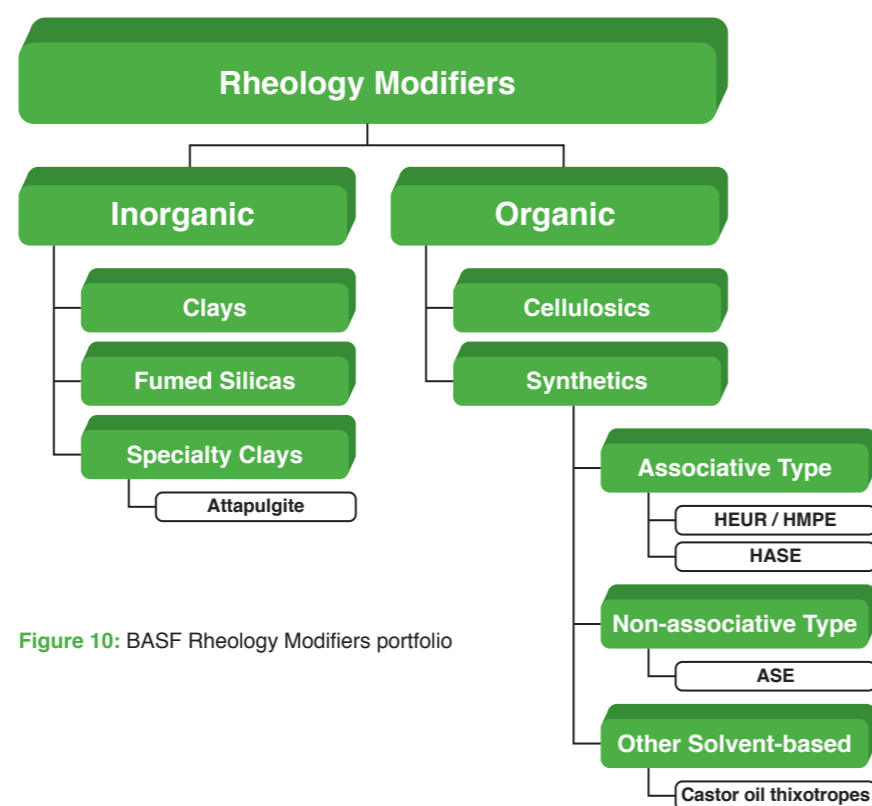


Figure 10: BASF Rheology Modifiers portfolio

BASF's Rheology Modifiers Product Range

BASF Rheology Modifiers For Water-based Systems

BASF offers nearly all commercially used classes of organic rheological additives for water-based paints and coatings. Each product class has its own characteristic properties. Table 11 highlights the benefits and areas of use of each product class. The following chapters will give you further insights on the advantages of BASF's rheology modifiers including detailed product recommendations for several application areas.

- **Rheovis® AS:**
Alkali swellable emulsions (ASE) for water-based paints & coatings
- **Rheovis® HS:**
Hydrophobically modified alkali swellable emulsions (HASE) for water-based paints & coatings
- **Rheovis® PU:**
Non-ionic associative thickeners based on hydrophobically modified polyurethane derivatives for water-based paints & coatings
- **Rheovis® PE:**
Non-ionic associative thickeners based on hydrophobically modified polyether derivatives for water-based paints & coatings
- **Attagel®:**
Inorganic thickeners and suspending agents made from specially processed attapulgite, a hydrated magnesium aluminosilicate

Property / Influence on	Polyurethanes, Polyethers (Rheovis® PU, Rheovis® PE)	Acrylics (Rheovis® AS, Rheovis® HS)
Low shear viscosity	Medium contribution	High contribution
High shear viscosity	High contribution (High film thickness by roller/brush application possible)	Low contribution, less impact on film thickness
Spattering	Improves spattering	Low effect
Gloss	Low to no effect	Matting effect possible
Influence of surfactants	Low to high, must be tested in each case	Hardly any (AS) Moderate (HS)
Syneresis	Tendency to syneresis	Low to no tendency to syneresis depending on type
Scrub and wash resistance	Very good effect	Good to moderate effect depending on type

Figure 11: Benefits and limitations of polyurethane/polyether and acrylic rheology modifiers

BASF's Rheology Modifiers Product Range

Non-ionic Associative Rheology Modifiers (Rheovis® PU, Rheovis® PE)

The Rheovis® PU and PE series of associative thickeners represent a class of ground-breaking materials based primarily on hydrophobically modified polyether and polyurethane derivatives. With these thickeners, it is possible to create a wide variety of rheological profiles, imparting superb attributes to a broad range of water-based paints and coatings.

The rheological behavior of aqueous paints and coatings can be rendered either more Newtonian (brush, roll-on, curtain coating) or more pseudoplastic (sprayable) in nature to ensure optimized application properties. These thickeners are water-soluble or water-emulsifiable polymers with a segmented structure. The basic framework consists of polyethylene glycols, hydrophobic alcohols and diisocyanates or other linking groups (Fig. 12).

Polyurethane and polyether chemistries open up many possibilities for synthesizing thickeners with differing property profiles. This can be achieved, for example, by varying:

- the type of hydrophobic end group
- the molecular weight of the thickener
- the degree of branching of the polymer

The strength of the physical network and the resulting rheological properties of the system can be controlled via the type of the hydrophobic end groups. Long hydrophobic end groups exert strong interactions and ensure efficient thickening at low shear rates.

The length of the hydrophobic group influences not only the strength of the associative effect but also the kinetics of exchange and thus the rate at which the associative linkage points break and reform. So, the type of the hydrophobic modification has a direct impact on the thickening profile of the associated rheology modifiers (Fig. 13).

- **Key benefits for your formulation:**
 - Broad rheology profile
 - Highly efficient across many resin types
 - pH independent
 - Improved wash and scrub resistance
 - Low impact on water uptake
 - Low impact on water whitening
 - Excellent leveling
 - Reduced spattering
- **Limitations:**
 - Other components (surfactants, solvents, polymer dispersions, pigments) can influence thickener performance

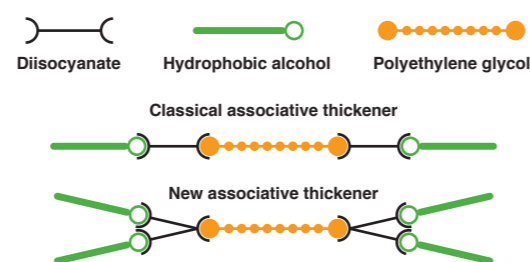


Figure 12: Schematic drawing of Rheovis® PU polyurethane thickener chemistry

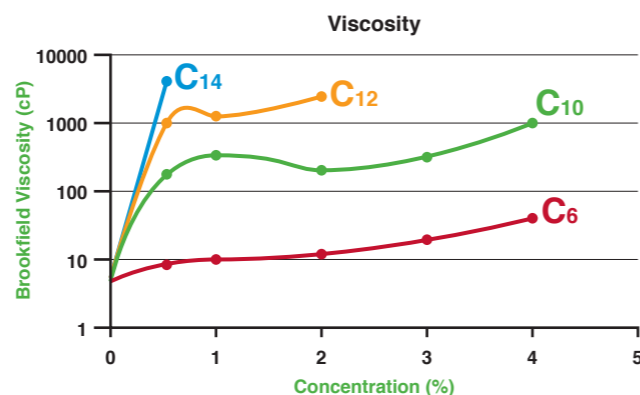


Figure 13: Influence of length of hydrophobic modification on viscosity development of associative rheology modifiers

When compared with non-associative thickeners, associative thickeners produce a more favorable (i.e. more Newtonian) rheology profile. Unlike polyacrylate thickeners, Rheovis® PU and Rheovis® PE products are pH-independent and have minimal affect on water sensitivity. Offering low molecular weight and controlled elasticity, they invariably and markedly reduce spattering. These associative thickeners ensure excellent rheology control for easier handling and application. The result is environmentally sound waterborne interior and exterior paints and varnishes offering enhanced consumer appeal.

As always, where several components are required to work together in a system, the following potential "conflicts" have to be taken into consideration (Fig. 14):

- **Surfactants:** Because associative thickeners have the character of surfactants, they compete with other surfactants such as emulsifiers within the system. These interactions can affect viscosity as well as leveling, gloss and hiding power.
- **Organic solvents:** Also, organic solvents can influence the thickening performance of associative thickeners. In general, hydrophobic solvents (e.g. mineral oils) do increase the thickening effect. More polar solvents (e.g. butyl glycol) can decrease the thickening performance.
- **Particle Size of Polymer Dispersions:** The bigger the surface area of an aqueous polymer dispersion the more interactions of an associative thickener with the polymer particles are possible. That is the reason why a smaller particle size polymer dispersion is beneficial for the thickening performance of an associative rheology modifier.
- **Dispersants:** Polyacid-type dispersants can interact with non-ionic associative thickeners, decreasing solubility.
- **Pigments / pigment concentrates:** Rheovis® PU and Rheovis® PE thickeners are compatible with a wide variety of pre-dispersed pigments. Reduction in viscosity is, however, sometimes observed ("viscosity loss on tinting").
- **Other thickeners:** In most cases, blends of only two to three thickeners are required to obtain the desired rheological profile.

Our Rheovis® PU and Rheovis® PE products are designed to readily ensure the required viscosity profile. They offer easy application and produce finishes of the highest quality, making them ideal for advanced water-based architectural, industrial and marine paints. BASF's Rheovis® PU and Rheovis® PE thickeners are of low viscosity so that a direct addition into the aqueous based formulation under moderate shear rate is recommended.

In principle, addition of the thickener can be done at any stage of the paint manufacture. It is common practice that the thickener is added either just before the let-down or at the end of the paint manufacture. Since associative thickeners are surface active components, care should be taken while incorporating into sensitive formulations to avoid destabilization of the dispersion paint. Combinations of high shear thickeners with other low and mid shear thickeners – or other types of thickeners, e.g. cellulose ethers – can be used to attain the desired balance of the rheology profile.

BASF Rheovis-type thickeners help to provide high quality finishes. To optimize their impact on paint, formulators have to consider the particle size and surface-chemistry of the dispersion, the surfactants and the co-solvents used in the paint in order to avoid undesired effects.

Summary:

Rheovis® PU and PE associative rheology modifiers offer a series of advantages over other commonly used thickening agents:

- Possibility to create a wide variety of rheological profiles; effective across many resin types
- Easy to roll and spray
- Improves application properties
- Optimized flow, leveling and sag resistance

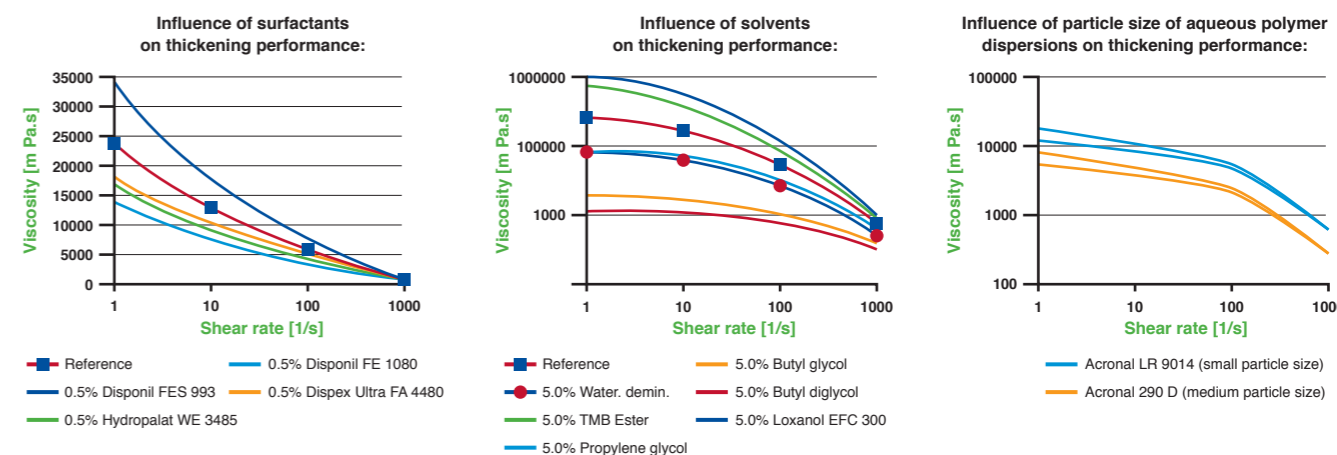


Figure 14: Influence of surfactants, solvents and particle size of aqueous polymer dispersions on associative rheology modifiers performance

BASF's Rheology Modifiers Product Range

Acrylic Rheology Modifiers (Rheovis[®] HS, Rheovis[®] AS)

Alkali Swellable Emulsions (ASE) are dispersions of acid functional acrylic polymers in water. They are supplied at low pH and the acid groups on the polymer chains need to be neutralized to allow the polymer to swell and thicken.

Under acidic conditions the polymer has a tight, coil-like structure and after the addition of alkali to the system, the pH increases and the acid functional groups on the thickener begin to dissociate. As a result, the thickener becomes more water-soluble and starts to uncoil. As the pH increases further, the polymer takes on a more open long-chain structure, leading to entanglement of thickener molecules with each other. This results in an increase in viscosity and is pictured schematically below:

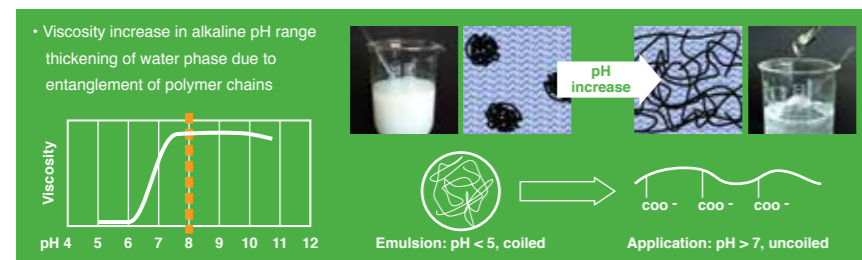


Figure 15: Neutralization of alkali swellable emulsions leads to swelling of polymer particles and viscosity increase ("hydrodynamic thickening")

The concentration of acid groups, the molecular weight and degree of crosslinking of the polymer are important factors influencing the rheology profile and thickening efficiency of acrylic thickeners.

HASE (hydrophobically modified alkali swellable emulsion) associative thickeners are also commonly found in latex paints. HASE thickeners differ from ASE products in that they also contain long-chain hydrophobic groups in addition to acid groups distributed throughout the polymer chain.

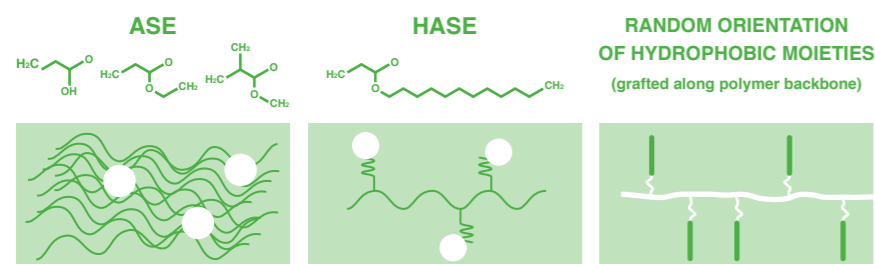


Figure 16: HASE thickeners are – similar to ASE thickeners – based on a polyelectrolyte backbone but have additional pendant hydrophobic groups.

▪ **Limitations:**

- pH sensitivity
- Ca⁺⁺ ion sensitivity
- Limited water and scrub resistance
- Water whitening

▪ **Summary:**

ASE / HASE rheology modifiers offer a series of advantages but also limitations for aqueous paint and coating systems

▪ **Key benefits for your formulation:**

- Strong shear thinning effect (pseudoplasticity)
- Anti-settling and anti-sag properties
- Excellent spray properties
- Good viscosity stability after tinting
- Easy handling; low viscosity
- pH sensitivity
- Ca⁺⁺ ion sensitivity
- Limited water and scrub resistance
- Water whitening

HASE-type thickeners are obtained when hydrophobic moieties, referred to as associative monomers, are copolymerized into the polymer backbone of an ASE-type thickener. Similar to ASE-type thickeners, HASE polymers thicken at a pH above 7 through repulsion of carboxylate anions along the polymer backbone. However, HASE polymers present enhanced viscosity because the hydrophobic groups aggregate together in the water phase in a manner similar to the way in which surfactants form micelles. These 'hydrophobic modifications' can associate either with each other on an intra- or intermolecular basis or in combination with other hydrophobic materials, especially latexes and surfactants in a coating formulation. This is why they are often referred to as 'associative' thickeners.

Compared to hydrophobically modified polyurethane thickeners (HEUR), HASE thickeners have a higher molecular weight, are ionic, and have a lower hydrophobe density (i.e. hydrophobe number per molecular volume). Because of this, HASE thickeners are somewhat of a hybrid thickener, deriving some of their efficiency from hydrophobic interactions and some from molecular volume effects traditionally utilized by non-associative thickeners (e.g. ASE).

In practice, HASE have become widely accepted as rheological modifiers, not only because of their technical performance in the coating sector such as good flow and leveling, freedom from roller spatters, etc., but also because of their cost attractiveness. The performance of the rheological modifiers can be fine-tuned in choosing the appropriate hydrophobe moiety. HASE rheology modifiers are less 'shear-thinning' or conversely more 'Newtonian' than ASE rheology modifiers.

BASF's ASE and HASE thickeners are usually supplied as low viscosity emulsions and at 25 - 45% solids depending on grade. They are easily mixed into aqueous-based systems and in many cases can be added directly to the system to be thickened followed by pH adjustment where necessary. The final pH of the thickened formulation should generally be in the range 8.0-9.5 to ensure optimum thickening efficiency and maintenance of a stable viscosity. If a volatile alkali such as ammonia is used, care should be taken to avoid loss of the alkali and lowering of the pH as viscosity reduction may occur. In some cases, it may be necessary to dilute the thickener (up to 2:1 with water) before addition to certain latex systems to avoid any localized thickening and instability.



BASF's Rheology Modifiers Product Range

Hydrated Magnesium Aluminosilicate (Attagel®)

Attagel® attapulgite rheology modifiers by BASF offer a wide range of performance benefits in many liquid systems. Attagel thickeners and suspending agents are made from specially processed attapulgite, a hydrated magnesium aluminosilicate and a principal member of the fuller's earth family of clay minerals having the ideal formula: $3MgO - 1.5Al_2O_3 - 8SiO_2 - 9H_2O$.

Attapulgite occurs as tightly packed bundles of submicron particles whose lath-like structure gives it unique colloidal and sorptive properties. Attagel rheology modifier is an ultra-fine mineral containing bundles of sub-micron particles. When the bundles are well dispersed in liquid systems, the colloidal particles interact to form a network that entraps liquid and smaller particles and suspends larger particles (Fig. 18).

Attagel rheology modifiers are exceptionally effective gellants, thixotropes and suspending agents that provide consistent performance over a wide range of liquid systems. Manufacturers use them in place of more expensive rheology agents, wholly or partially, to gain the many benefits they offer during a product's life cycle.

Attagel thickeners and suspending agents provide benefits including easy dispersion, formulating latitude and long-term stability. The colloidal network forms a thixotropic gel that if undisturbed, is stable indefinitely. Under modest shear, however, the structure breaks down and the liquid becomes thin and flowable. When agitation ceases, the scattered particles realign to reform the colloidal network and thicken the liquid. The cycle of thinning and thickening, by changes in shear, can be repeated endlessly.

As a leader in attapulgite technology, BASF manufactures Attagel products using methods we pioneered and continue to develop. We engineer quality into these products by starting with a high-grade attapulgite mineral and processing it under strict control. The mineral is mined from our holdings in southwestern Georgia and northern Florida, USA which contain some of the purest attapulgite available. We then unlock the potential of this versatile mineral by purifying the crude and manufacturing a variety of products through well-controlled heat treatment and particle-size processing.

Attagel rheology modifiers are hydrated grades made by low-temperature drying. They are specially processed to create submicron-size particles with selected residue and moisture specifications for optimal dispersing and gelling capability.

Attagel thickeners develop high viscosity when they are well dispersed. This involves breaking up the attapulgite aggregates and distributing the particles evenly in the fluid. In water-based coatings, Attagel products are usually added at the end of the pigment-grind step to prevent absorption of surfactants that can cause over dispersion and hinder gel formation. The mix should have enough water so it remains in the proper viscosity zone, for near maximum shear, as viscosity increases. In solvent-based systems, where a surfactant is needed to disperse the hydrophilic Attagel particles, the Attagel product should be added early to ensure capture of the surfactant.

High-speed mixing creates rapid thickening. Intensive, slow-speed mixing, such as with a double planetary-type mixer, may take longer to develop near maximum viscosity and may require more solids to generate adequate shear. Since shear rate is more critical than mixing speed, low-speed mixers can be used with the proper order of addition, or with a pregel.

Pregelling Attagel products take advantage of the shear inherent in particle crowding. Manufacturers often use pre-made Attagel concentrates if not enough shear can be applied to the main mix batch. Pregels are especially useful in formulations that foam when mixed rapidly or if high-speed mixers are unavailable. They are also added to systems with abundant liquid and relatively small amounts of pigment and vehicle.

Many processes use Attagel pregels that contain 10% to 15% solids. These are formed under low-to-moderate mixing.

Summary:

Attagel products offer distinct advantages over other commonly used thickening and suspending agents

- During formulation, Attagel colloidal clays disperse easily in aqueous and solvent-borne systems
- Attagel products provide wide latitude in formulating as they are essentially inert and compatible with most additives and tolerate most physical and chemical environments
- Attagel products need no special solvents, activators or modifiers, except in solvent-borne systems where a surfactant is recommended
- In end-use applications, Attagel rheology modifiers assist in syneresis control, sag resistance, film build, leveling, spatter resistance, spreadability, feathering, tint strength and hiding
- During storage, Attagel products reduce liquid separation (syneresis), do not swell, are stable over wide pH and temperature ranges, are insoluble in organic liquids, and generally resist settling

Figure 17:
Electron micrograph of
Attagel® inorganic
particles

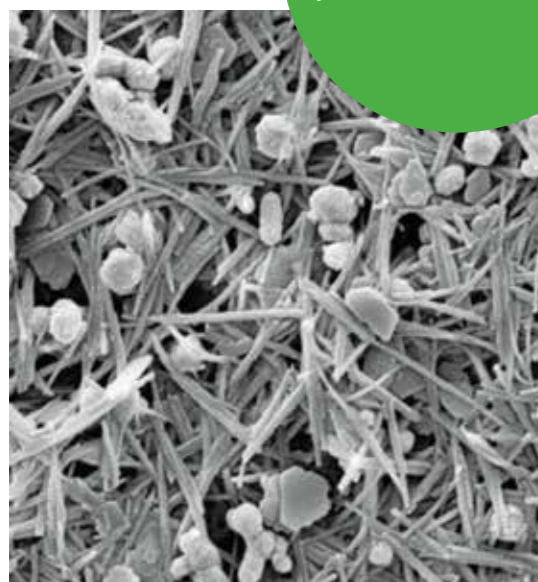
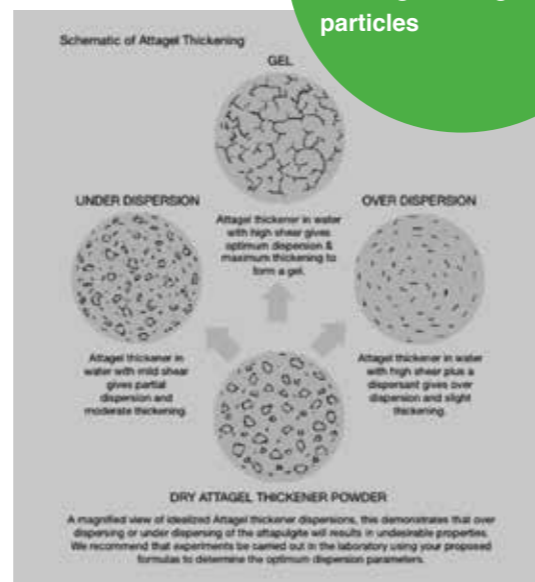


Figure 18:
Schematic representation
of thickening mechanism
of Attagel® inorganic
particles



BASF's Rheology Modifiers Product Range

BASF Rheology Modifiers for Solvent-based Systems

Efka® RM:

Organic thixotropes based on hydrogenated castor oil for non-aqueous paints & coatings (former Rilanit® brand)

To control the rheology or increase viscosity in solvent-based coatings, many different organic and inorganic active substances are used. Hydrogenated castor oils, like Efka® RM 1900 and Efka® RM 1920 (former Rilanit® special at micro and Rilanit® HT extra), offer a strong thickening effect in different coating systems. At the same time, these products produce high thixotropy so that greater film thickness can be applied. Sagging of thick films on vertical surfaces is effectively prevented while working and flow properties are also improved. Pigment settling is substantially reduced as well. Efka® RM 1900 and Efka® RM 1920 are both micronized powders. The usage and working mechanics are shown below:

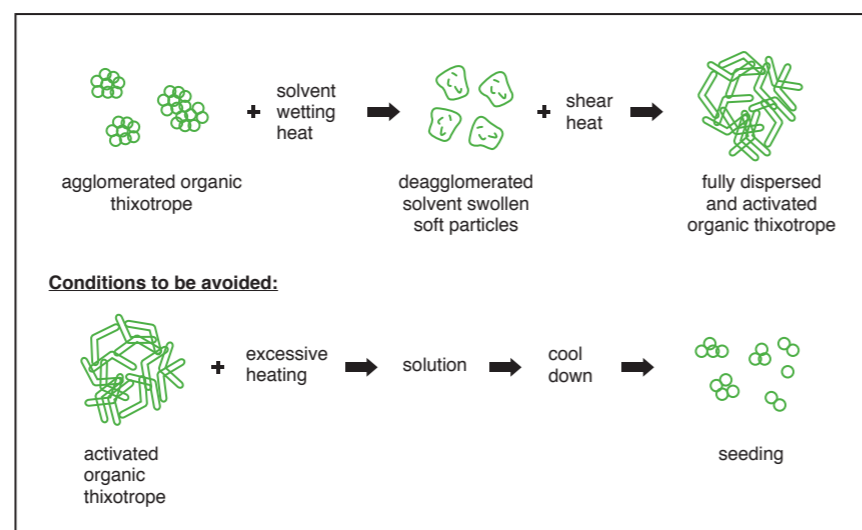


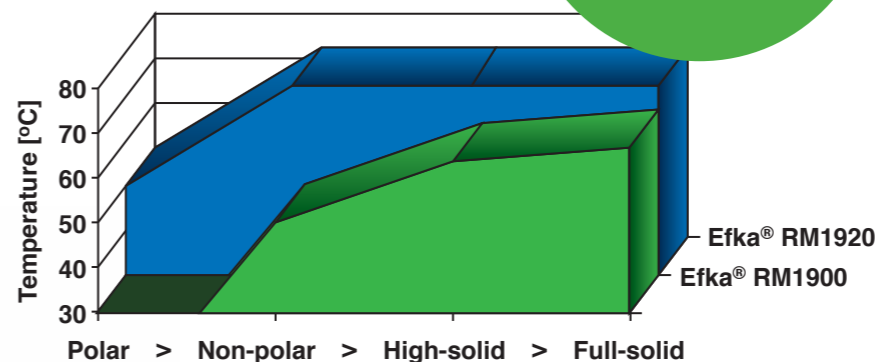
Figure 19: Working mechanism of Efka® RM thixotropes in solvent-based coatings and conditions to be avoided.



Optimum results can be obtained if the following processing instructions are followed: -

- Preferably a pre-gel is prepared in high speed grinders. The addition is usually made in powder form, where it is beneficial to predisperse the thickener for approximately five minutes in the solvent-binder mixture, prior to pigment addition.
- Temperature limits: Efka® RM products have different temperature limits which are also influenced by the polarity of the solvents as shown in the diagram below. To ensure proper dispersion of the thickening agent, it is essential that certain temperature limits are observed and sufficient shear forces to ensure adequate dispersion are generated.
- Stirring alone is not sufficient to achieve adequate homogenization, even if the thickener is added in a pre-gelled form. The shear forces usually generated in dissolvers, pearl mills or similar grinding equipment, are generally sufficient to obtain the degree of dispersion required.

Figure 20: Temperature dependency of Efka® RM thixotropes in solvents with different polarity



Summary:-

- Efka® RM products are organic thixotropes based on hydrogenated castor oil for non-aqueous formulations
- Offer a strong thickening effect in different coatings, while at the same time Efka® RM products produce a high thixotropy
- Sagging is effectively prevented while working and flow properties are improved, with pigment settling substantially reduced
- Sufficient shear forces are needed to ensure adequate dispersion of Efka® RM powders, and preferably a pre-gel is prepared in high speed grinders prior to pigment addition
- Certain temperature limits have to be observed
- Efka® RM 1900 tolerates relatively high working temperatures

Formulation challenges and product recommendations

BASF offers a broad range of mainly organic rheology modifiers, each one designed for specific application areas and customer requirements.

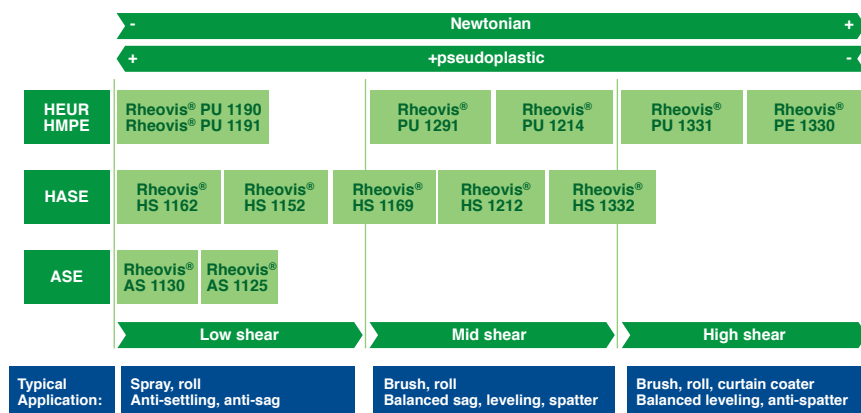


Figure 21:

BASF product recommendations for organic rheology modifiers for water-based systems and their corresponding shear profiles.

HEUR: Hydrophobically modified polyurethanes

HMPE: Hydrophobically modified polyethers

HASE: Hydrophobically modified alkali swellable emulsions

ASE: Alkali swellable emulsions

Typical challenges customers encounter while formulating paints are:

- **Leveling** – Good leveling is needed to ensure a smooth finish, to avoid brush marks.
 - High shear thickeners help to improve leveling.
- **Brush drag** – A well balanced brush drag is needed to provide perfect hiding power.
 - Mid shear thickeners help to adjust the “resistance” needed to process the paint.
- **Sagging** – Sagging leads to gravity-driven irregularities in thickness and can be prevented by rendering the paint pseudoplastic behavior.
 - ASE-type thickeners provide optimal anti-sagging behavior.
- **Spattering characteristics**
 - Associative thickeners allow for low spatter characteristics.
- **Anti-settling** - Homogenous distribution of components of paint allow for a ready-to-use paint without stirring / mixing.
 - Attagel provides convincing anti-settling characteristics.

A. Rheology control in aqueous systems, low shear thickening, strong pseudoplasticity

Rheovis PU 1191

Latest generation strong low shear thickener with excellent performance and easy handling. Strong pseudoplasticity VOC-free.

Rheovis PU 1190

A highly effective, non-ionic rheology additive with high thickening properties at low shear stress to form a pseudoplastic viscosity.

Rheovis HS 1162

Acrylic thickener with associative thickening; strong thixotropic flow behavior; low water uptake; no impact on wet adhesion even after long water contact; highly recommended for non-dripping stains and paints

Rheovis HS 1152

Acrylic low shear thickener with associative thickening for paints and plasters; improves anti-sagging; prolongs open time.

Rheovis AS 1130

Non-associative pure acrylic thickener; highly efficient low shear thickener; high shear thinning, anti-sagging and anti-settling; used in pigment and filler slurries but also highly successful in industrial and automotive formulations for spray applications.

Rheovis AS 1125

Non-associative pure acrylic thickener; alkali swellable emulsion (ASE); low shear thickener; high shear thinning; anti-sagging; high yield point; lower water uptake.

Rheovis HS 1169

Acrylic low shear thickener with associative thickening; suitable for spray applications; less water uptake; prolonged open time.

B. Rheology control in aqueous systems, mid shear thickening, medium to low pseudoplasticity

Rheovis PU 1291

VOC-free, odor-free, associative thickener that shows high efficiency in ICI viscosity at lower dosage. This well-balanced mid-shear rheology modifier allows for improved hiding power and excellent film appearance. It is suitable for all types of aqueous paints and coatings: premium flat & eggshell, semi-gloss and gloss coatings.

Rheovis PU 1214

A non-ionic mid shear thickener for aqueous systems, low structural viscosity, polyurethane polymer. Nearly Newtonian, excellent balance of high and low shear viscosity build.

Rheovis HS 1212

Hydrophobically modified alkali swellable emulsion (HASE) for high quality waterborne systems where good flow and leveling are required. Improves flow; excellent efficiency; all-round product which can be used in most paint systems.

C. Rheology control in aqueous systems, high shear thickening, Newtonian

Rheovis PU 1331

Heavy metal-, solvent- and VOC-free solution of polyurethane in water. Latest generation high shear thickener. Ultra efficient, best in class ICI performance.

Rheovis PE 1330

Newtonian rheology modifier for aqueous coatings. Features include excellent flow and leveling properties, excellent application hiding, excellent spatter resistance, good gloss development, and excellent shelf-life of coatings.

D. Rheology control in non-aqueous systems

Efka RM 1920

Efka® RM 1920 offers a strong thickening effect in different coating systems. It produces a high thixotropy so that higher film thickness can be applied. Sagging of thick films on vertical surfaces is effectively prevented while working and flow properties are also improved. Efka RM 1920 tolerates relatively high working temperatures which are particularly evident wherever the solvent consists mainly of white spirit. It shows optimum temperature stability in coatings based for instance on air-drying alkyd resins.

Efka RM 1900

Micronized powder offering a strong thickening effect; high thixotropy, anti-sagging, improved working and flow properties.