Rheological Additives

TEGO® ViscoPlus

Panta Rhei – Greek for everything flows – certainly applies to paints and coatings. From manufacture through storage and processing to drying or curing after application, many different demands are made on a coating or printing ink, related to its flow properties. Characteristics which are affected include:

- settling/sedimentation (important for storage stability)
- brushing resistance
- spattering
- sprayability
- sagging
- flow

In solventborne formulations, the flow properties can be completely regulated via the molecular weight of the dissolved binder. In waterborne formulations, the binder is in the form of dispersed polymer particles so that regulation of the flow behavior by changing the molecular weight is not possible. Rheological additives (thickeners) must therefore be used to adjust the flow properties of waterborne coatings and printing inks.

Rheologie

Rheology (Greek: rheos = flow or streaming, logos = word/science) is the study of deformation and flow of substances. Flow is the continuous deformation of a material under the influence of external forces. Various rheological measuring methods can be used to characterize coatings.

The quantities measured in rheological investigations are forces, deflections and velocities. Viscosity is the resistance of a liquid to forced, irreversible change of position of its volume elements.

Energy must be supplied continuously to maintain the flow of a liquid. Viscosity η, the most frequently used rheological parameter, is calculated from the shear rate $\dot{\gamma}$ and the shear stress τ. Basic rheological parameters are explained in terms of the two-plate model (fig. 1).

The upper plate of area A is movable and the lower plate stationary. The plates are separated by a distance h which is filled with liquid. When a certain force F is applied the upper plate reaches a velocity v which is related to the shear stress.

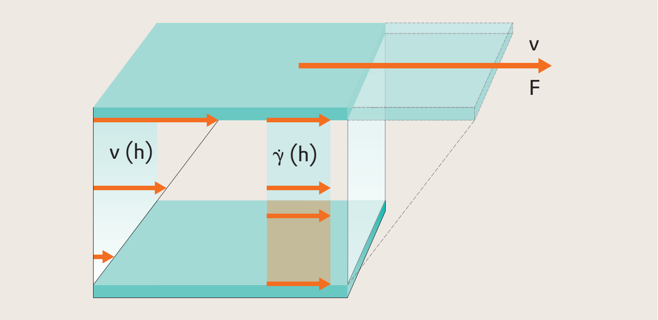


Figure 1: Flow in the gap between two horizontal parallel plates moving relative to each other.

The two characteristic values, shear stress, τ, and shear rate, $\dot{\gamma}$, can be derived from the two-plate model. The shear stress has the dimensions of pressure and is defined as the shear force F [N] per shear area A [m^2] where the force is parallel to the surface. The unit is the Pascal (Pa) which is the same as N/m^2.

$$\text{Shear stress } (\tau): = \frac{F}{A} \left[\frac{N}{m^2} = Pa \right]$$

The shear rate ($\dot{\gamma}$) or velocity gradient is obtained from the velocity v [m/s] and the plate separation h [m]. The units are $second^{-1}$.

$$\text{Shear rate } (\dot{\gamma}) = \frac{v}{h} [s^{-1}]$$

Although the term viscosity is often used in connection with coatings, the term flow behavior would surely be better. Usually coatings show a flow behavior in which they become thinner, that is to say, the viscosity value drops under the influence of shear forces. This phenomenon, known as pseudoplasticity, will be dealt with in more detail later.

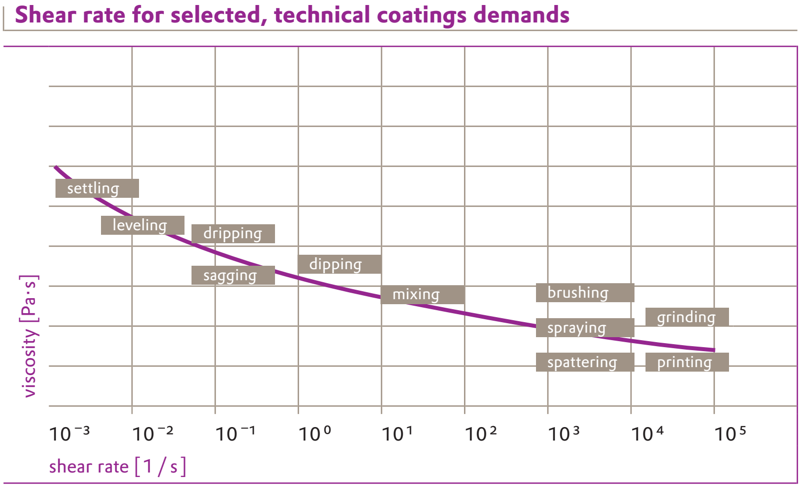

Shear rate for selected, technical coatings demands

Figure 2: Effect of shear rate on applicational properties

Applicational properties of coatings are associated with different shear rates (fig. 2). When stirring (dispersing), low viscosities are necessary but storage should preferably take place at high viscosity so that the pigments are prevented from settling out. For spray application, the paint should have as low a viscosity as possible but as soon as the paint is on the surface it should assume a high viscosity to prevent sagging on vertical substrates. The flow behavior of paints under typical processing conditions can be ordered according to shear rate.

Viscosity describes the frictional forces in a system and thus the resistance of a liquid to flow. The viscosity is a measure of the viscous flow of a liquid. The larger the viscosity, the less flowable the liquid. The (shear) viscosity (dynamic viscosity) is obtained as the ratio of shear stress τ to shear rate $\dot{\gamma}$. The units are $Pa \cdot s^{-1}$.

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

If the viscosity of a substance is constant at different shear rates, it is said to exhibit ideal or Newtonian behavior. Newtonian flow is generally found only with low molecular weight liquids such as water, solvents and mineral oils. In practice, most shearable systems have flow properties which depend on the shear rate.

If the viscosity decreases with increasing shear stress, the flow behavior is said to be intrinsically viscous, shear thinning or pseudoplastic. Most coatings and polymer solutions show pseudoplastic behavior.

Bingham fluids are viscoplastic but their flow properties are linear. After a minimum shear stress, they reach the yield point, τ_f, and begin to flow. Below this point they behave as an elastic body. Examples are ketchup and certain wall

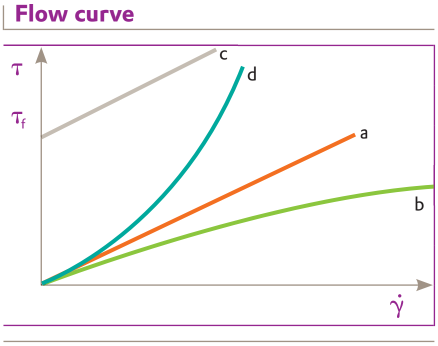

Flow curve

Figure 3

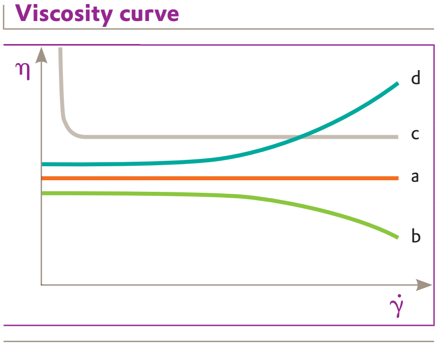

Viscosity curve

Figure 4

a) Newtonian behavior
b) pseudoplastic (non-Newtonian) behavior
c) Bingham behavior with yield point τ_f
d) thixotropic behavior

paints. These liquids only begin to flow when a particular stress is reached. This occurs, for example, if a loaded paint roller is pressed against a wall and rolled. At that moment, the shear force is sufficient for the paint to become liquid and wet the wall. As long as the paint is on the roller without any force applied it behaves like an elastic solid and does not drip from the roller.

Materials whose viscosity increases with increasing shear stress are thixotropic or dilatant. Thixotropic behavior is shown by, for example, dispersions with high solids content or high polymer concentrations. Thixotropic behavior is not usually found in paints and coatings as it can lead to problems with processes involving pumping or stirring.

Flow behavior can be shown diagrammatically in two ways: as a flow curve or a viscosity curve. A flow curve shows the dependence of shear force τ on shear rate $\dot{\gamma}$ (fig. 3) and a viscosity curve shows how the viscosity η depends on the shear rate $\dot{\gamma}$ (fig. 4).

Rheological additives can be roughly separated into inorganic and organic thickeners or thickeners for solventborne or waterborne coatings.

Examples of modified inorganic thickeners for solventborne and waterborne systems include:

- bentonite
- synthetic lattice-layer silicate
- pyrogenic silica (sometimes organically modified)

Examples of organic thickeners for solventborne or waterborne systems include:

- polyureas
- cellulose derivatives
- polyamides

Examples of organic thickeners for waterborne coatings include:

- associative thickeners
- non-associative thickeners

This list is not intended to be comprehensive.

Associative thickening involves non-specific interactions of hydrophobic end-groups of a thickener molecule both with themselves and with components of the coating. The thickener produces a reversible, dynamic network of thickener molecules and other components of the coating. The thickening effect is caused by interactions of the hydrophobic end groups of the thickener with other components of the formulation.

Non-associative thickening is thickening by an entanglement of water-soluble, high molecular weight polymer chains. The effectiveness of a thickener is mainly determined by the molecular weight of the polymer. Formulations thickened non-associatively have pseudoplastic rheology with highly elastic properties. This produces good stabilization against settling out and low sagging even with high build coatings. Non-associatively thickened systems often have limited flowability. The high molecular weight of the thickeners can sometimes lead to compatibility problems such as depletion flocculation

Associative thickeners also consist of hydrophilic water-soluble or water-emulsifiable polymer components and can simultaneously act in a non-associative manner. Both thickening modes are exhibited by associative thickeners, albeit to different extents. Table 1 shows thickeners commonly used for waterborne coatings and the way in which the thickening is produced.

Associative thickening can produce rheology ranging from Newtonian to pseudoplastic. Associative thickeners are often used to adjust application properties such as spattering or brushing resistance. Formulations with associative thickeners often exhibit high gloss and good leveling.

Polyurethane thickeners belong to the associative category. The molecular weight of polyurethane thickeners is from one to several powers of 10 lower than that of non-associative thickeners. Non-associative thickening can therefore be ignored.

Chemistry of polyurethane thickeners

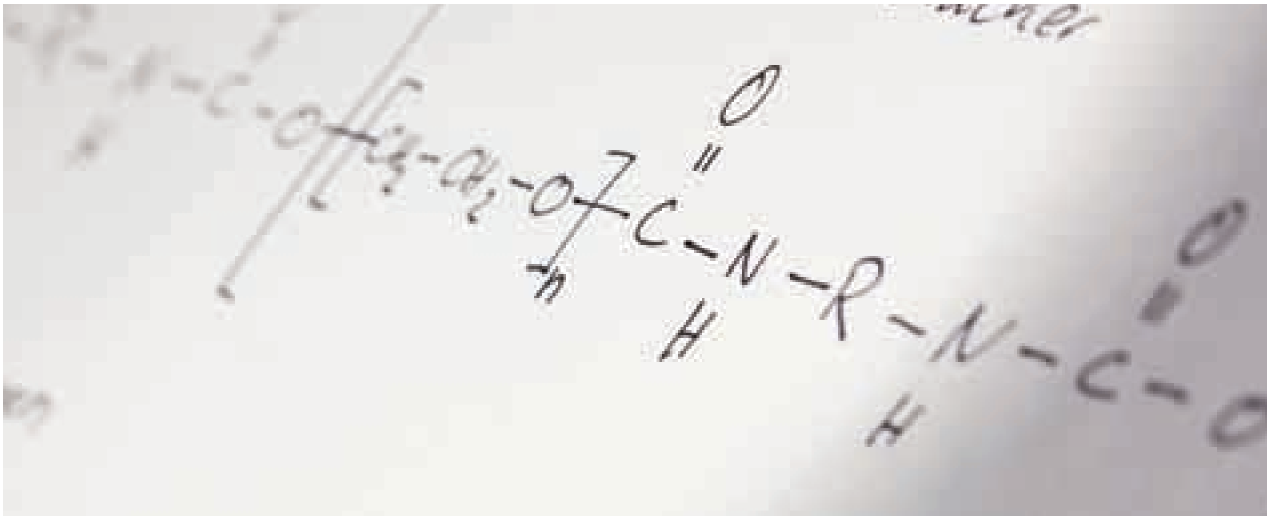
Polyurethane thickeners are water-soluble or water-emulsifiable polymers with a segmented structure. The middle section consists of one or more hydrophilic segments while the end-groups are hydrophobic. Linking of the middle segments with each other and with the end-groups occurs mainly via free hydroxyl groups of the segments with mono- or poly-isocyanates forming the urethane structures which give their name to this class of products. The molecular weights of typical polyurethane thickeners lie between 15,000 and 100,000 g/mol.

Overview of different classes of thickener and the method by which they thicken

Thickener	Associative thickening	Non-associative thickening
Polyurethane thickeners ″HEUR“	yes	negligible
Polyacrylate thickeners	no	yes
Hydrophobically-modified polyacrylate thickeners ″HASE“	yes	yes
Hydrophobically-modified polyether thickeners ″HMPE“	yes	
Cellulose ethers	no	yes
Hydrophobically-modified cellulose ethers ″HMHEC”	yes	yes

HEUR:	**H**ydrophobically modified **E**thylenoxide **U**rethane **R**heology modifier
HASE:	**H**ydrophobically modified **A**lkali **S**wellable **E**mulsion
HMPE:	**H**ydrophobically **M**odified **P**oly**E**ther
HMHEC:	**H**ydrophobically **M**odified **H**ydroxy **E**thyl **C**ellulose

Table 1



Polyurethane chemistry opens up many possibilities for synthesizing thickeners with differing property profiles.

This can be achieved by, for example, varying:

- the type of hydrophobic end group
- the molecular weight of the thickener
- the hydrophilic character of the middle section by the choice of isocyanate and the molecular weight of the polyethylene glycol
- the middle section with hydrophobic dialcohols
- the branching of the thickener molecule by reaction with polyisocyanates or polyalcohols
- the branching of the middle section by reaction with alkyl epoxides during manufacture of the polyethylene glycol

Further variations are possible during the formulation of the thickener as a waterborne preparation. Substances high in hydrophobic components require emulsifiers or solvents as formulation aids. The structure of the emulsifier co-determines the applicational properties of the thickener. A suitable choice of emulsifier allows the property profile of the thickener to be adjusted.

Mode of action of polyurethane thickeners

The associative thickening action of polyurethane thickeners can be explained as follows: interactions of the thickener molecules with each other and with the surface of dispersion and pigment particles produce a network (fig. 5).

Although the simplified model in fig. 5 is helpful in explaining associative thickening clearly, the actual mechanisms of thickening by polyurethane thickeners are more complex.

Investigations on solutions of polyurethane thickeners in water show that the thickener molecules are present in monomolecular form only in highly diluted solutions. With increasing concentration, the thickener molecules associate with each other to form loop micelles. The block-like structure of the thickener favors this phenomenon:

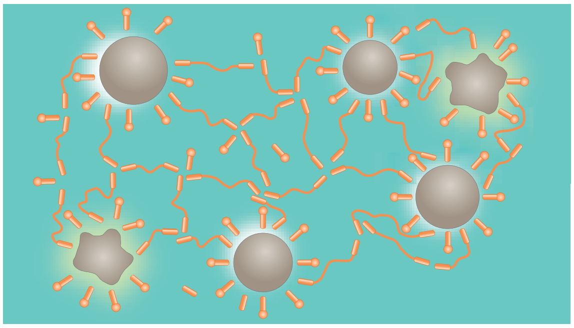


Figure 5: Mode of action of polyurethane thickeners

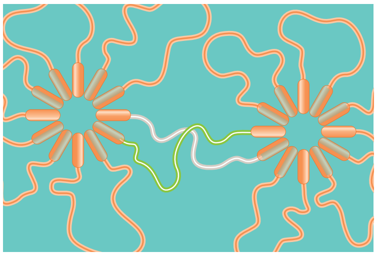


Figure 6: Bridging

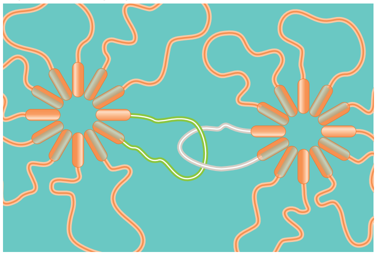


Figure 7: Entanglement

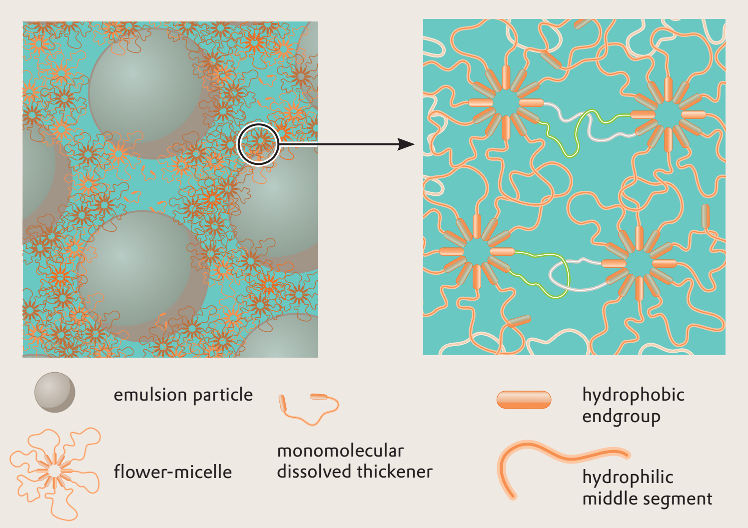


Figure 8: Associative thickening via thickener gel

the hydrophobic components of the molecule orient towards the interior of the micelle, the hydrophobic middle segments form the outer loop-shaped sheath.

At even higher concentrations, mutual interaction of the loop micelles results in two phase systems consisting of a free-flowing phase with low thickener content and a thickener gel. In the free flowing phase, the thickener molecules are dissolved individually or are present as loop micelles. The thickener gel consists of associates of thickener molecules. The cohesion of the gels is thought to stem from bridging and entanglement mechanisms by the micelles (fig. 6 and 7).

If the concentration of thickener in aqueous solution is raised still further, the two phase system changes into a single phase thickener gel.

In paints, polyurethane thickeners are usually used at concentrations at which two-phase systems have been observed in aqueous solutions. It is therefore probable that the polyurethane thickener is also present in paints as a two-phase system. The thickener gel interacts via the hydrophobic groups with the surfaces of the pigments and binders. A refined model of the mechanism of associative thickening by polyurethane thickeners is shown in fig. 8.

Polyurethane thickeners form a temporary network. The linkage points of the network consist of thickener molecules and thickener micelles adsorbed on the pigment or binder surfaces. It is characteristic that the linkage points of the network are constantly breaking and reforming. The system is thus highly fluid which explains the good flow and leveling characteristics of associatively-thickened paints.

The strength of the network and the resultant rheological properties of the system can be controlled via the hydrophobicity of the end groups. Long hydrophobic end groups exert strong interactions and ensure efficient thickening. To achieve comparable thickening with shorter end groups, significantly higher concentrations are required.

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. When shear stress is applied to paints, the associative linkage points are broken. If the thickener is unable to reestablish the disrupted linkage points immediately, the associative network is weakened. There is then a shear-rate-dependent loss in viscosity.

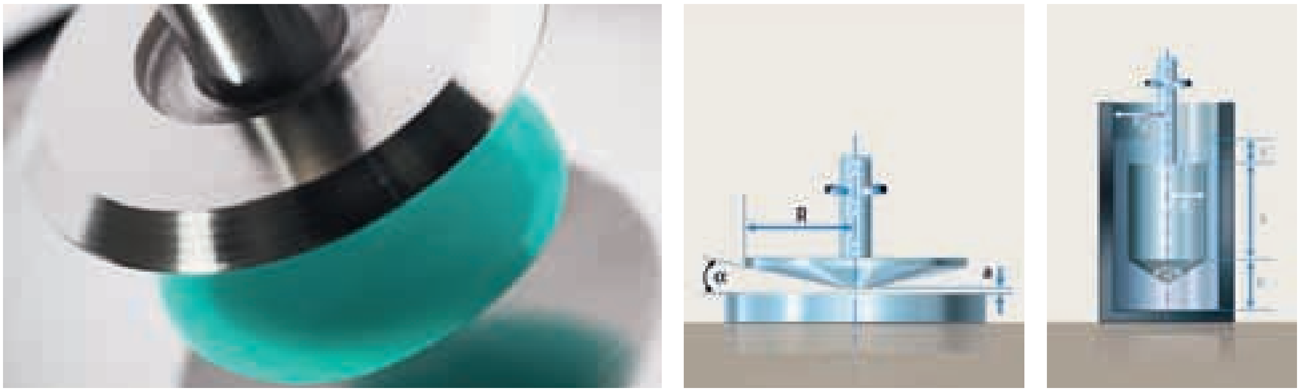


Figure 9: Example for an absolute viscometer and various measuring cells

Long hydrophobic end groups possess a slow rate of exchange; i.e. the viscosity of thickeners with long hydrophobic end groups diminishes slowly under shear stress. The formulation becomes pseudoplastic. Short hydrophobic end groups exhibit a fast rate of exchange so that thickeners with such groups are effective even at high shear rates and result in formulations with Newtonian rheology.

Test methods

Measuring viscosity with the absolute viscometer

In absolute viscometers, the geometry of the measuring cell is known and the shear surface and plate separation are therefore also known. The shear stress, shear rate, and thus the viscosity can be calculated from the shear force and speed. The absolute viscometer is usually used to take measurements over a range of shear rates. The results are presented in flow curves or viscosity curves. Typical absolute viscometers are cone and plate or two-plate rotational viscometers (fig. 9).

Measuring viscosity with the relative viscometer

The volume of the sample is unknown; shear rate and shear stress cannot be quantified. Relative viscometers are suitable for comparative measurements of systems with similar rheology. In the coatings industry, relative viscometers of the Brookfield or Stormer spindle type are commonly used, usually at constant shear force.

Leveling

Leveling, the flow behavior in a horizontal position, is determined with a leveling doctor blade. In this method, the coating is applied as five double lines with increasing film thickness from 100 to 1000 µm on a Leneta sheet. The proportion of lines which have coalesced is quoted according to a scale of 0 (no leveling) to 10 (very good leveling). It is also common practice to visually compare a dried paint film with a standard (fig. 10). The paint is usually applied in a manner resembling subsequent application conditions.

Figure 10: Bad and good flow after brush application

Sagging

Sagging, the flow behavior in a vertical position, is determined with a sagging doctor blade. Ten stripes of the paint are applied using the doctor blade in thicknesses of 75 to 300 µm on a Leneta sheet. Immediately after application, the card is lifted into a vertical position so that the stripes lie parallel to the horizontal. The stripes with the lowest film thickness are at the top. After drying, the stripe at which the paint starts to sag is given on a scale of 0 to 10: 0 meaning that all stripes sagged and 10 meaning that no stripes sagged (fig. 11).

Alternatively, it is possible to determine at which film thickness sagging starts to occur by applying the paint, in various thicknesses or as a wedge, to a vertical surface.

Brushing resistance

Brushing resistance is determined by applying a specified amount of paint to a test surface and assessing the resistance felt on distributing the paint with a brush.

Spattering characteristics

The spattering characteristics can be determined by applying a specified amount of paint uniformly on a previously conditioned roller and rolled several times over a grid. The paint spray thrown from the roller is collected on a black card under the grid. The test card is compared with a standard tested at the same time.

These test methods are shown in a video on our Homepage entitled "Various methods for measuring viscosity".

FAQs

For which paint formulations is TEGO® ViscoPlus suitable?

TEGO® ViscoPlus is only recommended for thickening waterborne coatings. The thickening effect is based on the interactions of the additive with pigment and binder particles. Thus, TEGO® ViscoPlus can basically be used in all waterborne emulsion paint formulations. The main areas of application are architectural coatings, wood finishes, printing inks and leather coatings.

Can all TEGO® ViscoPlus types be combined with each other?

All TEGO® ViscoPlus types can be combined with each other. If the required rheology cannot be achieved with one thickener, a combination of types with differing rheology profiles is recommended.

How can a rheology profile be finely adjusted?

If the required rheology profile cannot be achieved with one thickener, several thickeners can be combined. All TEGO® ViscoPlus types can be combined with each other. The rheology of the combination always lies between the profiles of the types used.

Can I combine TEGO® ViscoPlus with thickeners which have a different chemical composition?

Basically, combinations with the polyacrylate or cellulose ether thickeners commonly used in waterborne paints are possible. However it is recommended that


Figure 11:
Sagging test

the compatibility of the thickener in the formulation is checked.

How do the various TEGO® ViscoPlus types differ?

The thickeners differ in the rheology they produce in the application system:

TEGO® ViscoPlus	Rheology
TEGO® ViscoPlus 3000	Newtonian
TEGO® ViscoPlus 3010	Newtonian with high thickening at high shear rates
TEGO® ViscoPlus 3030	pseudoplastic
TEGO® ViscoPlus 3060	strongly pseudoplastic

What are the advantages of combining TEGO® ViscoPlus with polyacrylate thickeners?

Combination with polyacrylate thickeners enables the elastic viscosity of the paint to be increased. This leads to improved stability against settling and better sagging characteristics. Leveling is, however, frequently impaired.

What are the advantages of combining TEGO® ViscoPlus with cellulose ethers?

Combinations of cellulose ethers with polyurethane thickeners are usually encountered in architectural coatings with a high PVC. The cellulose ether imparts water retention to the paint and thus a sufficiently long open time. In addition the elastic viscosity of the paint is increased. Stability to settling and sagging characteristics are also improved. In many cases, however leveling and gloss are impaired by the cellulose ether.

What is the procedure if the rheology of a paint needs to be set using a combination of thickeners with differing rheology profiles?

With a pseudoplastic thickener, the rheology should initially be adjusted to a specified target value using low to medium shear rates. A Newtonian thickener is then added until the desired viscosity is achieved at high shear rates. The Newtonian thickener can also affect the viscosity at low to medium shear rates which should therefore be rechecked. If necessary the dosage of pseudoplastic thickener must be further adjusted.

Which types of binder can best be thickened with TEGO® ViscoPlus?

For a thickener network to form, the thickener must associate with hydrophobic surfaces. Effective thickening can be obtained with emulsifier-stabilized emulsions based on acrylates and styrene acrylates. Thickening with hydrophilic vinylacetate copolymers is less pronounced.

Why does the PVC influence the thickening effect of TEGO® ViscoPlus?

For a network to form, the thickener must associate with the hydrophobic surface of the binder particles. In paints with a high PVC, too few binder particles are available to form a strong thickener network.

How does the pH-value affect the thickening performance of TEGO® ViscoPlus?

In the typical range of pH for emulsion paints, the pH does not affect the thickening performance of TEGO® ViscoPlus.

Can a paint be made thixotropic using TEGO® ViscoPlus?

At high shear, the static viscosity of the pseudoplastic TEGO® ViscoPlus 3030 and 3060 falls. After the shear force is removed, the viscosity prior to shear is spontaneously reinstated. Thixotropy, in the sense of time-delayed increase in static viscosity, cannot be obtained with TEGO® ViscoPlus.

What are the ecological advantages of TEGO® ViscoPlus?

All grades are free of volatile organic compounds (VOC) and of alkylphenol ethoxylates (APE). No organotin catalysts are used in their manufacture.

Literature:
Edward J. Schaller, Peter R. Sperry
"Associative thickeners"
Handbook of Coatings Additives, Vol. 2,
edited by Leonard J. Calbo, pp. 105-164

Johan Bieleman "PUR-Verdicker"
Johan Bieleman, Lackadditive, Wiley-VCH,
pp. 51-59

Holger Reimann, Betina Joos-Müller,
Klaus Dirnberger und Claus D. Eisenbach
"Assoziativverdickern auf der Spur"
Farbe & Lack, 5/2002, pp. 44-55

Markus Schmidtchen, Thadeus Schauer,
Rolf Nothhelfer, Claus D. Eisenbach
"Dem Netzwerk auf der Spur"
Farbe & Lack, 2/2005, pp. 34-39