



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, related to its flow properties. Characteristics which are affected include:

- settling
- brush drag
- spattering
- 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.

Rheology

Rheology (Greek: rheos = flow or streaming) is the study of deformation and flow of substances. Various rheological methods can be used to characterize coatings.

The quantities measured in rheological investigations are forces, deflections and velocities. Viscosity, the most frequently used rheological parameter, is calculated from the shear rate and the shear stress. 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 is applied the upper plate reaches a velocity v which is related to the shear stress.

The two characteristic values, shear stress τ , and shear rate $\dot{\gamma}$, can be derived from the two-plate model. The shear stress is defined as the shear force F [N] per shear area A [m²].

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

The shear rate is obtained from the velocity v [m/s] and the plate separation h [m].

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

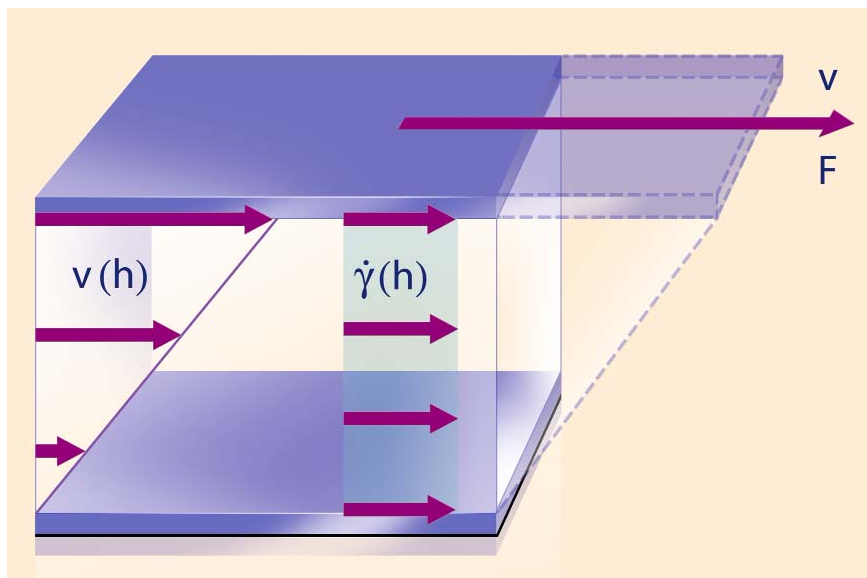


Figure 1: Two-plate model

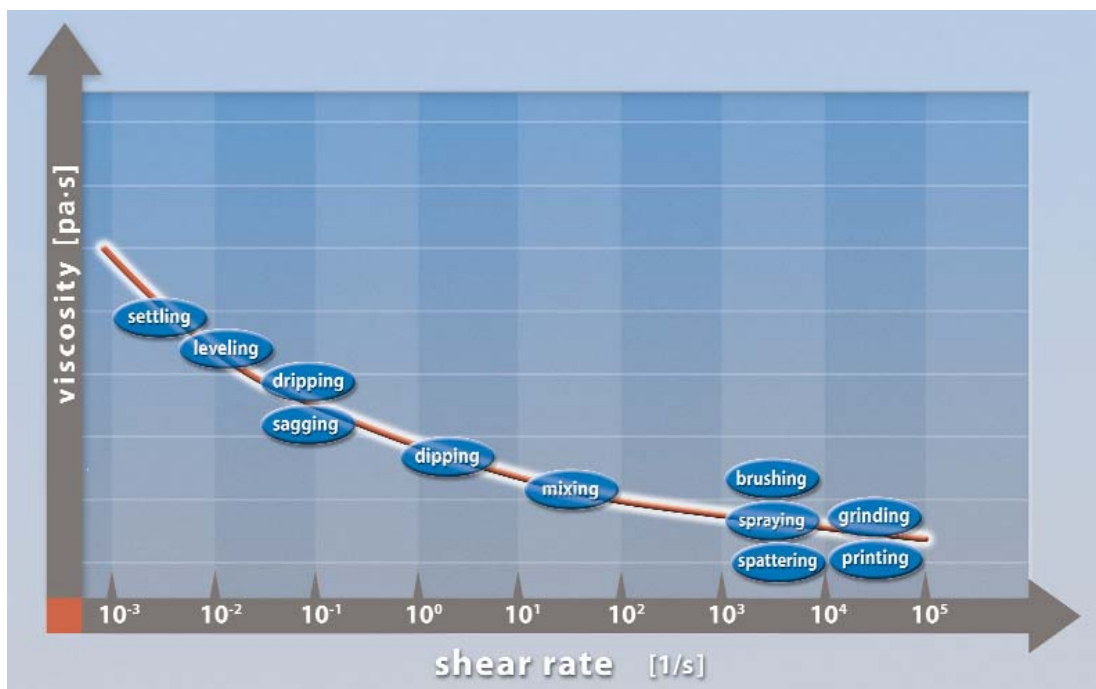


Figure 2:
Effect of shear rate on
applicational properties

Application properties in paints and coatings are associated with different shear rates (fig. 2) and the flow properties of coatings under different conditions also depend on shear rates.

Viscosity describes the frictional forces in a system and thus the resistance of a liquid to flow. The (shear) viscosity (dynamic viscosity) is obtained as the ratio of shear stress τ to shear rate $\dot{\gamma}$.

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

If the viscosity of a substance is constant at different shear rates, it is said to exhibit ideal or "Newtonian viscosity" 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 loading, the flow behavior is said to be shear thinning or pseudoplastic. Most coatings and polymer solutions show pseudoplastic behavior.

Materials whose viscosity increases with increasing shear loading are dilatant. Dilatant behavior is shown by, for example, dispersions 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.

Flow behavior can be shown diagrammatically in two ways: as a flow plot or a viscosity plot. A flow plot shows the dependence of shear force on shear rate (fig. 3) and a viscosity plot shows how the viscosity depends on the shear rate (fig. 4).

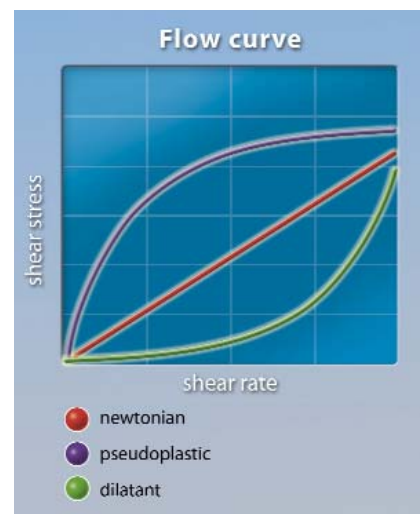


Figure 3: Flow curve

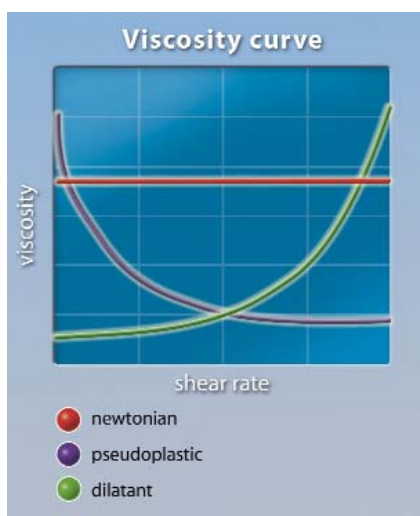


Figure 4: Viscosity curve

Thickening mechanisms in waterborne coatings

Two methods have been described for thickening waterborne coatings

- associative thickening
- non-associative thickening

Associative thickening, i.e. thickening by 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 with other components of the formulation.

Non-associative thickening, i.e. 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. For-

mulations 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 have limited flowability. The high molecular weight of the polymers can sometimes lead to compatibility problems such as depletion flocculation.

Associative thickeners also consist of hydrophilic water-soluble or 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 rheologies ranging from Newtonian to pseudoplastic. Associative thickeners are often used to adjust application properties such as spattering or brush drag. Formulations with associative thickeners often exhibit 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 groups with each other and with the end-groups occurs mainly via 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 und 100,000 g/mol.

The structure of a polyurethane thickener molecule is shown in fig. 5. The basic framework consists of polyethylene glycols with molecular weights between 3,000 and 10,000 g/mol and the repeating units linked with diisocyanates. The thickener molecules have end-groups which are usually either C₈ to C₂₀ alkyl- or aryl-groups. The relative amounts of

Table 1: Overview about most common thickener classes and corresponding thickening mechanisms.

Thickener	Associative thickening	Non-associative thickening
Polyurethane thickeners	yes	negligible
Polyacrylate thickeners	no	yes
Hydrophobic-modified polyacrylate thickeners	yes	yes
Cellulose ethers	no	yes
Hydrophobic-modified cellulose ethers	yes	yes

polyethylene glycol and isocyanate determine whether the middle portion offers left-over hydroxyl or isocyanate groups for reaction with the end-groups. If the middle section is synthesized with an excess of isocyanate, the non-reacted isocyanate groups can be used to react with hydrophobic alcohols or amines. If the middle section is made with insufficient isocyanate, the remaining hydroxyl groups can be used for reaction with alkyl monoisocyanates.

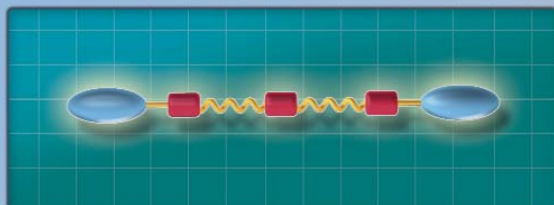
Polyurethane chemistry opens up many possibilities for synthesizing thickeners with differing property profiles. This can be achieved by, for example, varying:

- 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 part by reaction with alkylepoxides 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 codetermines the application properties of the thickener. Suitable choice of emulsifier allows the property profile of the thickener to be adjusted.

Typical Structure of a Polyurethane Thickener



Components




	= e.g. hydrophobic aliphatic residue $\text{CH}_3-(\text{CH}_2)_x-\text{O}-$ (x = 7-19)
	= e.g. hydrophilic segment of Polyethylenoxidopolyether $-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_y-$ (y = 70-200)
	= e.g. residue of an oligofunctional isocyanate $\text{R}-(\text{NH}-\text{CO}-)_z$ (z ≥ 2)

Figure 5:
Schematic structure of a polyurethane thickener

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 emulsion and pigment particles produce a network (fig. 6).

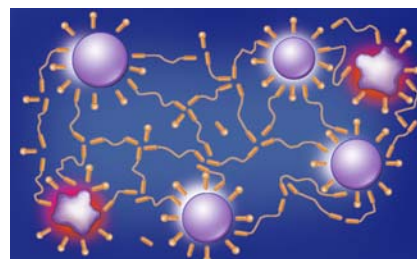


Figure 6: Mode of action of polyurethane thickeners

Although the simplified model 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: The hydrophobic components of the molecule orientate 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 a 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 (figs. 7 and 8).

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. 9.

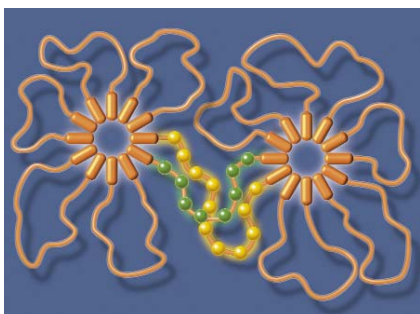


Figure 7: Bridging

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

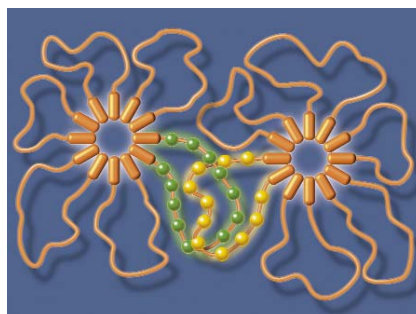
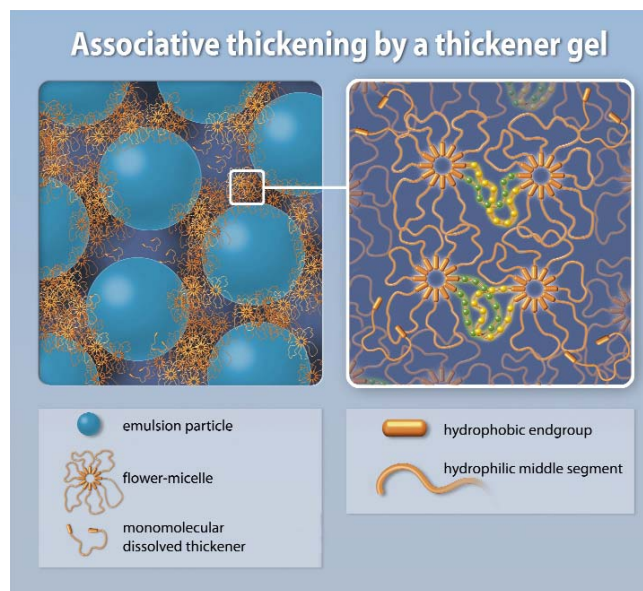


Figure 8: Entanglement

drophobicity 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

Figure 9:
Associative thickening
via thickener gel



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 hy-

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.

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 one range of shear rate. The results are presented in flow curves or viscosity curves. Typical absolute viscometers are cone and plate or two-plate rotational viscometers (fig. 10).

Measuring viscosity with the relative viscometer

The volume of the sample the shear force is applied 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 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 compare visually a dried paint film with a standard (fig. 11). The paint is usually applied in a manner resembling subsequent application conditions.

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

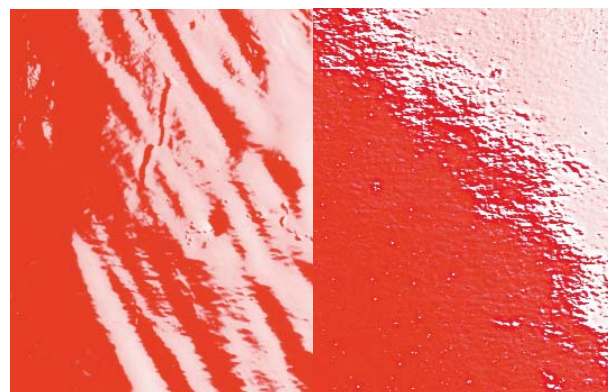


Figure 11:
Bad and good flow after
brush application

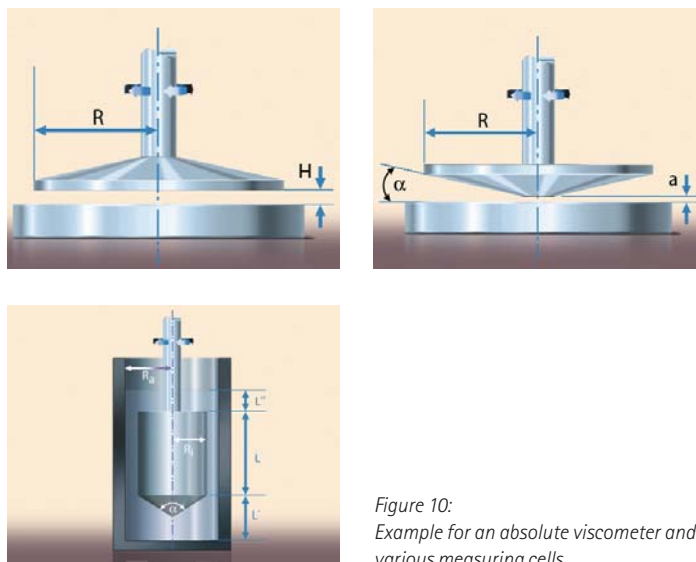


Figure 10:
Example for an absolute viscometer and
various measuring cells

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: all stripes sagged, 10: no stripe sagged).

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 (fig. 12).

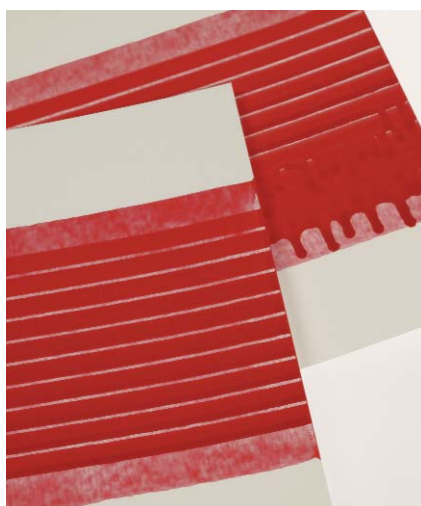


Figure 12: Sagging test

Brush drag

Brush drag 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 carton under the grid. The test card is compared with a standard tested at the same time.

Relating to the mentioned test methods please see the video "Measurement of viscosity (various methods)" on the enclosed CD-ROM.

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 the compatibility of the thickener in the formulation is checked.

Selection chart rheological additives

Product	Architectural coatings	Wood coatings	Industrial coatings	Others	Flow behaviour
TEGO® ViscoPlus 3000 ¹	•	•	•	•	Newtonian
TEGO® ViscoPlus 3010 ¹	•	•	•	•	Newtonian, high-shear
TEGO® ViscoPlus 3030 ¹	•	•	•	•	pseudoplastic
TEGO® ViscoPlus 3060 ¹		•	•	•	strong pseudoplastic

¹silicone-free

How do the various TEGO® ViscoPlus types differ?

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

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

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