

ELEMENTIS

A global specialty chemicals company

Application Leaflet

RHEOLATE[®] NiSAT technology

Technical background for non-ionic associative thickeners for aqueous applications

Key Benefits

- ❖ pH independent thickening
- ❖ Customize paint rheology
- ❖ Broad range of applications

Enhanced Performance Through Applied Innovation

Introduction

Elementis offers a variety of associative acting thickeners which are standard in the modern formulation of aqueous application, such as paints and coatings, adhesives, etc. These are the hydrophobic modified acrylic thickeners, often called HASE, and the NiSAT group of products. The term NiSAT, which is often used for this class of associative thickeners, abbreviates “**N**on**I**onic **S**ynthetic **A**ssociative **T**hickeners.

The HASE product group contains ionic, mainly anionic thickeners, which require pH proper adjustment for activation. This product group utilizes two mechanisms, water thickening and associative.

NiSAT product group, as mentioned, are already non-ionic and in principle used over the widest range of pH values. These products represent an advanced technology and are designed to give superior rheological characteristics so that many formulation requirements can be met. Depending on the product chosen, good leveling, spatter resistance, film build, and the flow characteristics can be achieved. The appearance of classic syneresis can even be minimized. Furthermore, NiSAT products do not need special activation so that the majority can be added to the letdown or even at the end of processing. This product class does not adversely affect the corrosion or the water sensitivity of the resulting system, and other secondary parameters such as gloss will not be negatively influenced.

In addition, all NiSAT grades available can be combined with each other and other product classes such as clays, cellulose ethers, or acrylic thickeners to obtain the customized rheology to meet the individual requirements (Figure 1).

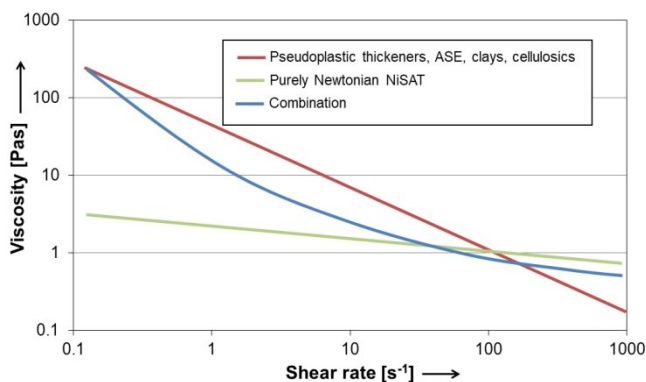


Figure 1: Comparison flow characteristics

Features

- Ability to customize paint rheology
- pH independent
- Good leveling
- Excellent spatter resistance
- Syneresis control
- Low influence on corrosion and water sensitivity
- Broad range of applications including glossy paints

However, the thickening response might be influenced by the chemistry of the binder used and its particle size as also by the type of fillers and pigments and their concentration. Further coalescents and surfactants have a tremendous affect on the thickener's effectivity.

Chemistry

This class of thickeners consists mainly of nonionic copolymers. The structure is schematically represented in Figure 2 and can be described as a minimum of two hydrophobic groups chemically bonded to a hydrophilic backbone. The water-soluble part of the molecule takes typically ~95% of the molecule weight. The total molecule weight of NiSAT's are typically in a range between 20000 and 50000 g/mol.

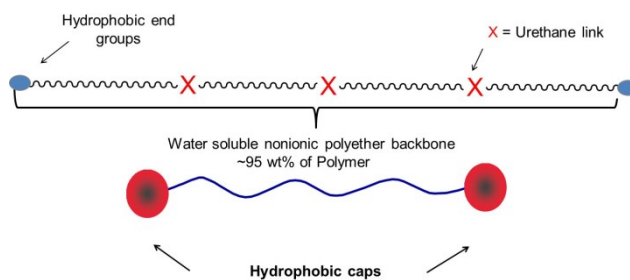


Figure 2: NiSAT chemistry

In principle, thickeners based on various chemistries such as polyether urea polyurethanes (RHEOLATE[®] 200 series and their low VOC counterparts, the RHEOLATE[®] 600 series as well as RHEOLATE[®] FX) or polyether polyols (the RHEOLATE[®] 300 series) are available. Polyether urea polyurethanes can be accurately described as hydrophobically modified ethoxylated polyurethanes. Polyether polyol-based grades do not contain urea or urea linkages and have a more branched structure.

As visible in the product overview in Figure 3, even more specialized chemistries to meet more specific requirements, have been recently developed. These are available as e.g. RHEOLATE[®] CVS or RHEOLATE[®] HX.

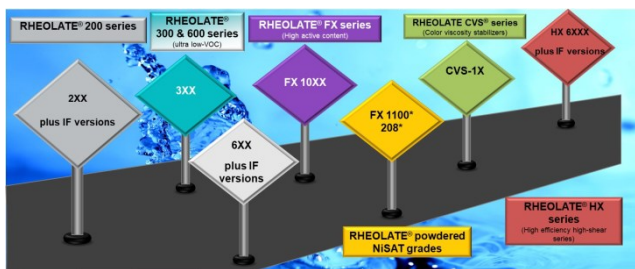


Figure 3: Overview available NiSAT product groups

The abbreviation CVS stands for “Color Viscosity Stabilizer” and represents a group of products of rheology modifiers providing outstandingly strong viscosity stability up on the tinter addition. This is often an issue, as a changing surfactant composition is often affecting the viscosity of the proposed system. Also, the polyether polyol based RHEOLATE® 300 series also acts quite stable under these conditions, however, to a lesser extent than RHEOLATE® CVS products.

To the RHEOLATE® HX product family belong a group of rheology modifiers which are acting with outstandingly high efficiency focussing on the high shear viscosity to meet the latest requirements of sustainable formulations.

Also powdered NiSAT grades RHEOLATE® 208 and RHEOLATE® FX 1100 are available. Both products consist of 100% active matter and are dedicated for formulation which need to be completely free of biocides and to meet the latest paint production requirements (modular concept, MOFA). Also, they are fitting into the latest sustainable market needs by reducing transport volume and cost.

In addition, the reduction of the biocide content was considered. Grades with the ending IF have been formulated “Isothiazolin Free.” They do not contain MIT or BIT.

All products mentioned in the individual groups offer specific flow characteristics which need to be selected in accordance with the requirements of the proposed final system. Therefore, they can be combined with each other or with different product classes.



As already briefly mentioned, all NiSAT grades use an associative mechanism which is schematically described in *Figure 4*.

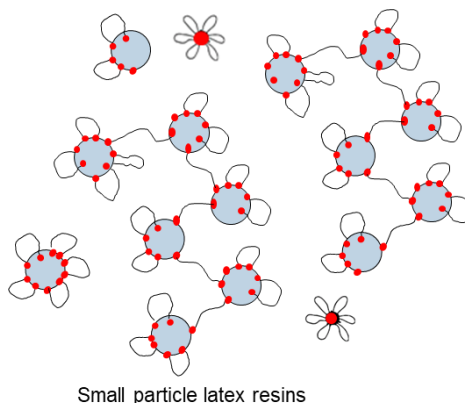


Figure 4: NiSAT network structure in latex systems

NiSAT thickener exhibit a surfactant like behavior. In water, the hydrophobic end groups will orient to each other forming micelles. As NiSAT molecules have hydrophobic end groups on either side, both will end up in the same micelle at low concentration forming loops. Due to interaction with themselves, the viscosity of NiSAT’s diluted in pure water rises high, sometimes too high for proper handling. Therefore, in such cases a controlled breakup of this network structure by appropriate dilutants is necessary. Note, these structures are transient due to thermal fluctuation (Brownian motion) and will always try to achieve a thermodynamic equilibrium. Also, the network can be disrupted by shear.

When NiSAT solutions are added to latex based, waterborne systems, their hydrophobic end groups will adsorb on the resin particles surface as visualized in *Figure 5*. Some fractions of the NiSAT molecule will have one hydrophobic end group adsorbed on one resin particles surface and the other on the neighboring particle surface. The resulting network consists of latex particles with an outer shell of thickener polymer. The rheologically active network is formed by a controlled “bridging” flocculation of resin particles with the NiSAT thickener on the particle surface acting as a glue.

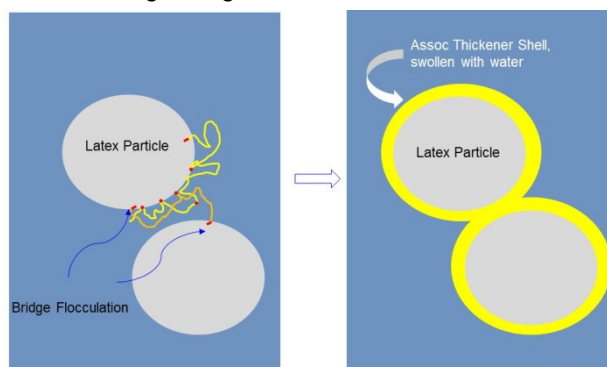


Figure 5: Hydration shell

The degree to which this happens depends on how much resin surface area is available. The surface area available in a typical acrylic resin is large enough that, at equilibrium, most of the hydrophobic end groups can be found adsorbed on the resin particles surface. Only a few floret-like micelles remain in solution.

In *Figure 6* varying stages of flocculation between the particles in a formulation are depicted from the left to the right.

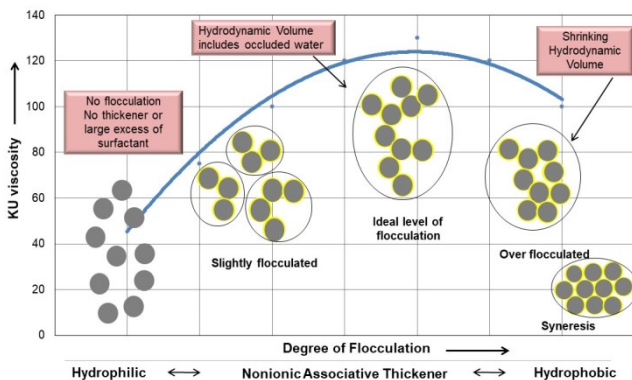


Figure 6: Controlled flocculation

Upon addition of a NiSAT thickener, latex particles will flocculate, providing fractal-like structures that occlude water. As this water is unavailable for the systems flow, the viscosity rises. The viscosity will continue to rise with the number of associations. The system is stable in the case that the rate of flocculation is equal to the rate of deflocculation.

With increasing hydrophobicity of the end groups of the thickener molecules and the number of bridging associations, the attraction forces between them and the latex surfaces rise. In parallel, the distance in between the particles is decreasing. From a certain point, the system is exceeding the ideal level of flocculation. A strong shrinkage of the hydrodynamic volume resulting in phase separation or even syneresis might result.

In the case of the majority of NiSAT products, the network has a relatively low elastic component so that it can relax at rest and thus provide excellent levelling. For the very hydrophobic grades providing very pseudoplastic flow, dominance of the elasticity might be the result due to the strong associations.

At the moment when shear is applied, the degree of flocculation decreases and continues to decrease more and more as the shear stress (or strain rate) increases. However, the NiSAT thickeners remain adsorbed on to the surface of the latex particle. This is likely the reason for the high viscosity additives provide at high shear rates (ICI viscosity).

As the properties of these purely associative technologies is mainly controlled by changing the frequency and the chemistry of hydrophobic units, available grades are acting differently with system components. Therefore, a change of the thickener chemistry can be a useful tool to overcome specific incompatibility issues.

However, the chemistry of the hydrophobic end groups also has a tremendous influence on the properties and the provided rheological characteristics. As visualized in *Figure 7*, very hydrophobic end groups are having a strong tendency to interact and to provide high viscosities at low shear with only small amounts of material formulated into the product.

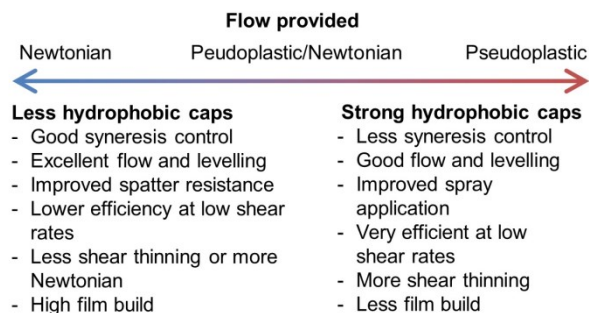


Figure 7: Influence of end groups

The rheology provided is strongly pseudoplastic for excellent spray applications along with excellent sag control, e.g. in industrial applications. Well-balanced levelling and flow characteristics are given. However, the effect on other properties like levelling, film build and roller spatter resistance up on brush/roller application or the reduction of real syneresis is less pronounced than with Newtonian NiSAT grades. These products are equipped with less hydrophobic end groups. The thickener molecules are interacting typically weakly with themselves and hydrophobic parts of the formulation. Therefore, they are usually being formulated at higher concentrations than pseudoplastic, hydrophobic grades. The flow provided is less shear thinning or Newtonian. However, as they are occluding similar amount of water per molecule, the hydrodynamic volume is larger and responsible for the increase of the viscosity at high shear. Newtonian NiSAT products do not build up elasticity, however, they do enhance the fluid character of the proposed system.

The described differences in chemistry result in the rheological characteristic shown in *Figure 8*. The rheogram displays the viscosity in Pascal seconds (Pas) on the vertical axis. The applied shear rate is plotted on the horizontal axis. A test system, a pure acrylic binder emulsion was equipped with different associative rheology modifiers to achieve equal mid shear viscosity determined by Krebs-Stormer (KU) viscometer. The product concentration necessary to adjust equal mid shear viscosity of 100 KU units was taken.

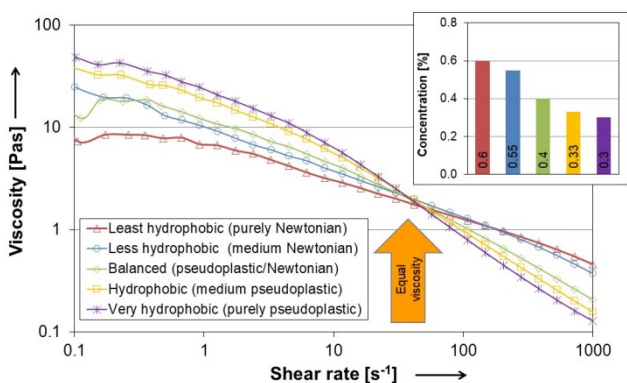


Figure 8: Effect of various NiSAT types on rheology

It becomes clear that the very hydrophobic thickener is providing the strongest shear thinning flow. In addition, the lowest product concentration is necessary to achieve the target viscosity. With reducing NiSAT hydrophobicity, the flow characteristics are moving from very pseudoplastic to Newtonian. The necessary NiSAT concentrations are increasing in the same way.

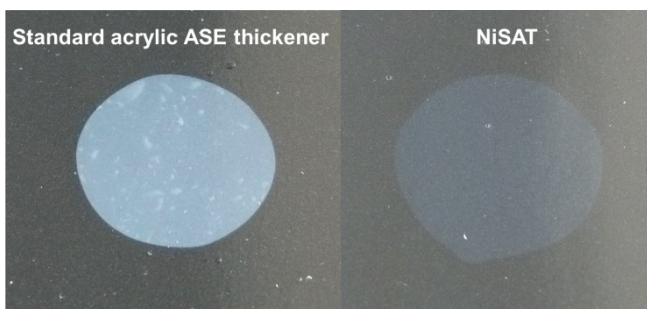


Figure 9: Influence on early water resistance

Due to the nonionic nature of the NiSAT molecules, the resulting film is less prone to water pick-up as with anionic grades e.g. acrylic thickener resulting in improved early water resistance (Figure 9) or anti-corrosion behavior.

Incorporation

The NiSAT chemistry has an influence on the potential incorporation methods. The liquid grades are all free flowing and can usually be added directly to the formulation under moderate shear. The ideal point of addition is after the millbase processing and before the binder addition in the letdown stage. However, these are surface active polymers and care should be taken in sensitive formulation to avoid shock or destabilization. This is especially relevant in cases of very hydrophobic products, such as RHEOLATE® 299. In such conditions a predilution might be beneficial to guarantee an immediate and smooth viscosity rise.

Other raw materials

Other raw materials in a formulation may have an influence on the performance and the effectivity of NiSAT grades. Specifically these can be coalescing agents, the binder emulsion and surfactants.

Even in low VOC formulations small amounts of co-solvents or coalescents are often being formulated e.g. to optimize the freeze-thaw stability. As visible in Figure 10, these can influence the viscosity. In the present example the influence of various coalescing agents on the mid-shear viscosity, in this case measured by Brookfield, in a pure acrylic paint formulation is taken.

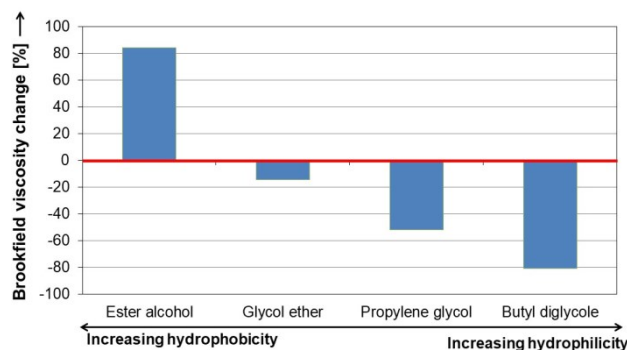


Figure 10: Coalescents influence on NiSAT efficiency

The rheology modifier has been used to achieve a certain Brookfield viscosity. The individually formulated coalescents have been added to the system at a concentration of 3%. The graph shows the Brookfield viscosity variation in comparison to sample without co-solvent.

While hydrophobic coalescents based on ester alcohol are causing a significant viscosity rise, the more hydrophilic examples, like propylene glycol and butyl diglycol, are causing a noticeable viscosity drop. Glycol ether only causes a slight viscosity change.

This effect has been attributed to the solvency of the micelle which weakens the associations and in extreme cases depresses the network dramatically. On the other hand, the effect can be utilized in a positive way. For instance, to fine-tune the flow properties especially if levelling needs a minor improvement. Hydrophobic, or even water immiscible, co-solvents, are causing the observed viscosity to increase by swelling the latices generating larger surface area for associations. Also, the associative polymer can become less soluble in the continuous phase and produce more micelles.

The binder emulsion used also has a big effect on the mid-shear viscosity which is mainly connected to the particle size of the binder particles emulsified which is visualized in *Figure 11*.

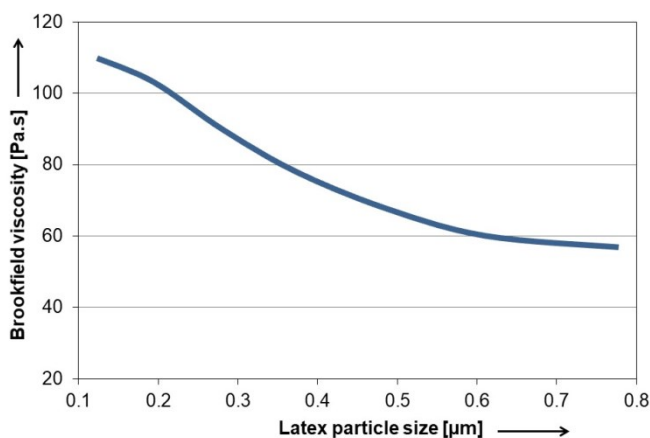


Figure 11: Effect of latex particle size

The highest viscosities can be achieved with small particle latices due to the larger surface area for interaction. In small particle emulsion, the associative thickeners with less hydrophobic end groups are offering the best flow. In large and medium size latices which are offering less surface area for associations, the more hydrophobic additives are recommended to effectively build up viscosity.

Similarly, the hydrophobic grades are best with latex systems that have a very hydrophilic surface. If the latex has a rather hydrophobic surface, then the Newtonian additives are giving the best flow.

Another product group with a large influence on the effectivity of NiSAT's are surfactants, wetting and dispersing agents. This is well known in the context of adding pigment pastes or colorant to paints. Pigment concentrates are typically rich on surfactants. As in most cases the colorants used are purchased and, the paint manufacturer has no influence on the surfactant composition. The result is often that the viscosity is dropping with increasing concentration of pigment concentrate as shown in *Figure 12*.

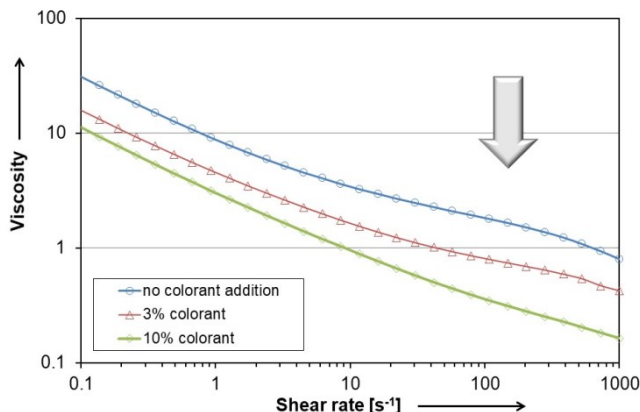


Figure 12: Surfactant addition via colorant

The described effect is normally dependent on the HLB value (hydrophilic-lipophilic balance; mostly relevant for nonionic surfactants) of the surfactant used. As shown in *Figure 13*, grades with an HLB value of around 10 produce the highest mid shear viscosities.

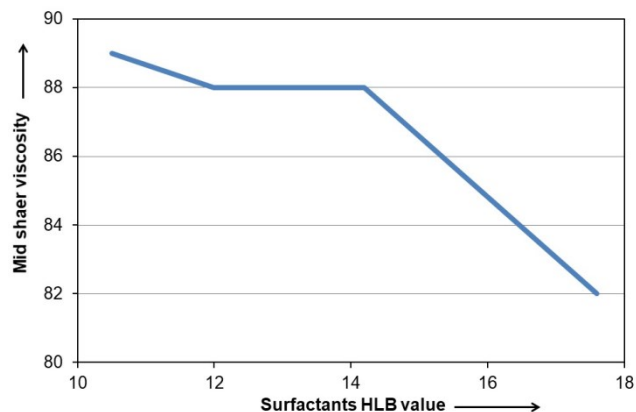


Figure 13: Influence of various HLB values

More hydrophilic surfactants with HLB values above 15 will generally reduce the viscosity. HLB values in between 10 and 15 are ideal for the use with purely associative thickeners.

The loss of viscosity with higher HLB nonionic surfactants is attributed to surfactant drift in the formulation. The added surfactant, e.g. by adding colorants, can displace the associative thickeners from their micelles. As they do not have associating unit, the network weakens and the viscosity drops (*Figure 14*).

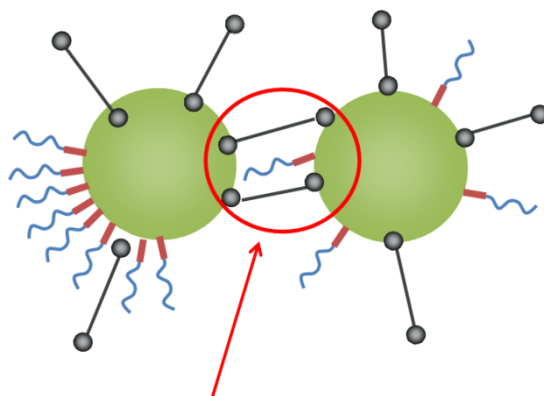


Figure 14: Network disruption by surfactants

Unfortunately, this effect might not occur immediately, but could be observed after several months of storage as the formulation gradually equilibrates. Therefore, storage stability studies are particularly important when evaluating associative thickeners.

In general, the NiSAT grades from the RHEOLATE[®] CVS product series or those based on a polyether polyol chemistry show the lowest sensitivity to the described surface and coalescent effects.

As also previously explained, NiSAT thickeners can be blended to meet precise flow requirements, levelling and roller spattering resistance, ideally balanced with the desired sag control.

Newtonian NiSAT

Figure 15 shows a practical example in a styrene acrylic pvc 50 paint. The rheograms are displaying the viscosity in relation to the shear rate. System contains 0.6% of a mid-range cellulose ether. As the cellulose ether is controlling mainly the low shear viscosity, a Newtonian NiSAT grade has been formulated in steps of 0.5%.

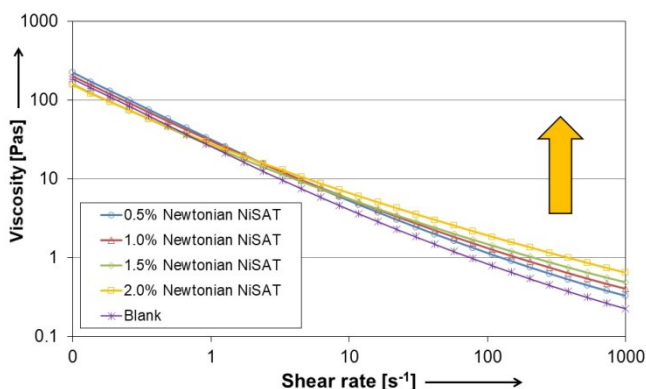


Figure 15: Newtonian NiSAT influence on flow

It becomes obvious that with increasing content of the formulated Newtonian NiSAT the viscosities at high and mid shear rates are rising in comparison to the blank sample which contains only cellulose ether. On the other hand, the viscosity on the lower shear side is almost unaffected.

However, an even more exact picture can be seen when performing a recovery test of the viscoelastic characteristics. The graph in Figure 16 shows the so-called damping factor, or tan delta, and has been plotted on the Y axis, while the strain, or deformation can be seen on the X axis in %.

Tan delta can be calculated as the factor out of G'' , the loss or viscous modulus, and G' , the storage or elastic modulus. If the tan delta value is above 1, the fluid characteristics are dominant. If the damping factor act below 1, the system is dominated by the elastic characteristics. In the shown graph, a tan delta of 1 is highlighted by the red line over the entirely tested strain range.

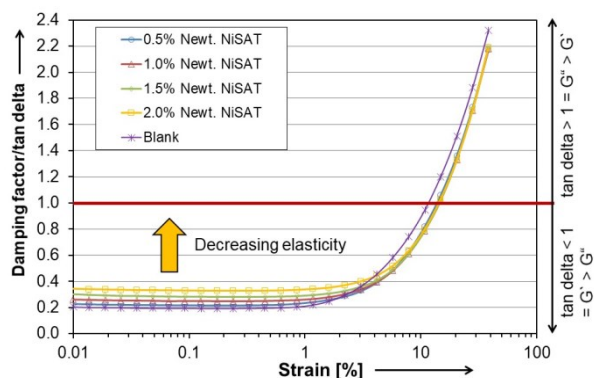


Figure 16: Newt. NiSAT influence on viscoelasticity

All samples show tan delta values far below 1 on the lower strain side which indicates a strongly elasticity behavior. Strain values in between 1% and 10% all curves showing an upwards swing of the slope. At strain rates between 10% and 11% all samples are crossing tan delta of 1 and the fluid character becomes dominant. So far, all samples are showing a similar picture. However, interesting differences can be seen when focusing on the low strain rates between 0.01% and 1%. In this range slightly upwards shifted damping factors can be detected with increasing concentrations of the Newtonian NiSAT. This behavior indicates that the use of the Newtonian associative thickeners is reducing the elasticity of the samples.

Performing a levelling test with the paints, shows improving performance with increasing content of Newtonian NiSAT (Figure 17).

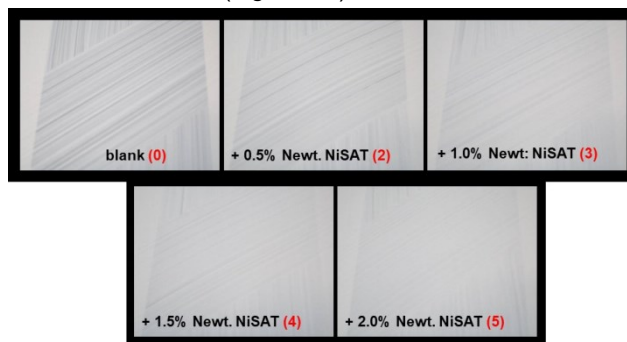


Figure 17: Brush-out levelling

In terms of roller spattering, the Newtonian NiSAT grades can also help to improve the performance. With increasing concentration of the rheology modifier, the number and the size of the spatters captured during roller application is reduced (Figure 18).

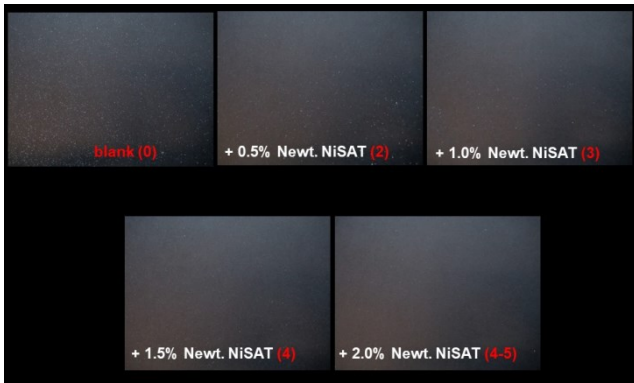


Figure 18: Roller spattering resistance

Consequently, it can be concluded that with increasing concentration of a Newtonian NiSAT the application behavior, such as levelling and roller spattering, can be significantly improved. These practical findings are also indicated by rheological finding such as increasing high shear viscosities and decreasing elastic character. The viscosity at low shear will only be minorly affected.

Pseudoplastic NiSAT

The following case study displays the effect of various pseudoplastic associative thickeners in a low pvc acrylic coating system. The viscosity of the individual samples has been adjusted to equal mid shear viscosities. In *Figure 19* the flow behavior is visualized as a rheogram.

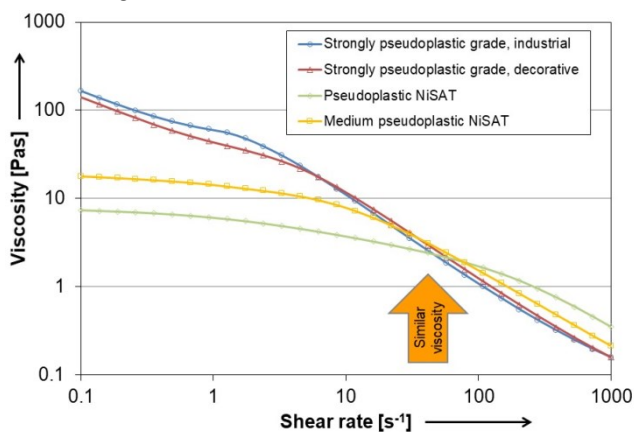


Figure 19: Pseudoplastic NiSAT flow character

It is monitored that the variously formulated pseudoplastic NiSAT's are imparting various low shear viscosities. Both grades are described as strongly pseudoplastic and provide the highest low shear viscosities and the strongest shear thinning flow character. The difference between both rheology modifiers is that the product dedicated for decorative application is very low in VOC, while the industrial grade is not free from VOC.

Both grades mainly find use in spray applied systems. The further tested associative thickeners are providing much lower viscosities at low shear rates. Especially the medium pseudoplastic additive provides the least shear thinning flow. The described flow behavior is also representing the hydrophobic character of the interactive end groups used in the rheologically active polymer. The strongly pseudoplastic grades are consisting of the most hydrophobic polymer end groups. With decreasing shear pseudoplasticity provided, the hydrophobicity is declining.

In terms of the viscoelasticity test monitors in *Figure 20* that the very hydrophobic, pseudoplastic acting grades are shifting the tan delta values to the range below 1. This is especially the case at low strain rates and indicates a dominant elasticity.

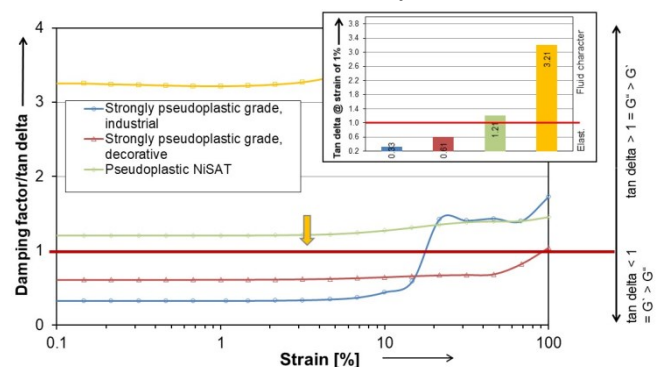


Figure 20: Pseudo. NiSAT influence on viscoelasticity

As it was mentioned, most of the NiSAT grades are only enhancing the viscosity and do not build up elasticity. This is the case with both products tested, marked as pseudoplastic and medium pseudoplastic. However, the result in the present study shows that with very hydrophobic polymers, implementation of strong elastic characters at very low stress is possible for improved storage stability, sag, and drip control.

Especially dripping of a paint during brush application or other handling is unwanted as it might caused spoilage of other surfaces. As visible in *Figure 21*, this can be limited to an absolute minimum by using a pseudoplastic NiSAT.



Figure 21: NiSAT effect on dripping

In systems equipped with a purely Newtonian associative grade this is not the case. The present results are showing another time when a combination of both thickener classes can help to achieve excellent applicability.

As pseudoplastic thickeners mainly find use in industrial applications, the effect on further properties of the final coating such as humidity and salt spray resistance is of major interest. As visualized in *Figure 22*, this thickener class does not have an adverse effect on these properties.

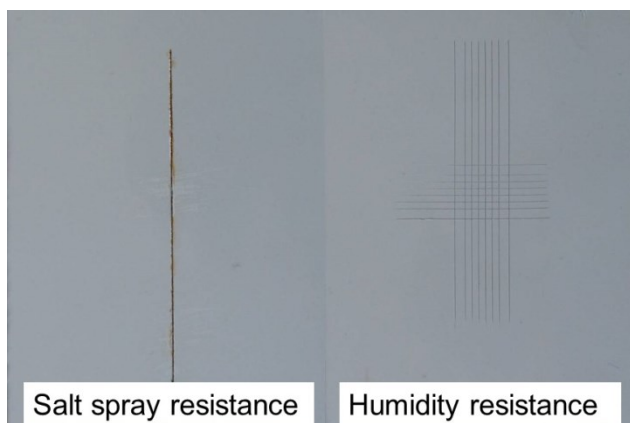


Figure 19: NiSAT influence on corrosion resistance

Conclusion

The displayed results show that the class of NiSAT thickeners offers many benefits in the formulation of a variety of industrial and decorative paint and coating formulations. The products are generally suitable for high quality systems including those with high gloss. The products in general do not have an adverse effect on the properties of the final, cured coating layer such as water and corrosion resistance. On the other hand, the rheological efficiency can be influenced by other raw materials such as binder type, coalescents and co-solvents.

Pseudoplastic grades interact strongly due to the hydrophobic nature of the end groups used in the molecule. This causes low shear viscosities, and depending on the product, also elastic characteristics. Therefore, this product is well suited for systems requiring strong sag control and storage stability as well as excellent sprayability.

Newtonian rheology modifiers contain less hydrophobic end groups in the rheologically active molecule and therefore act therefore less interactively. However, the large hydrodynamic volume typically provides high viscosities at high shear rates for excellent flow and levelling as well as a reduction of roller spattering. As this group of products is slightly reducing the elasticity of the final system a significant reduction of “real” syneresis” can be obtained. However, due to the usual low effect on mid and high shear viscosity, Newtonian NiSAT’s are typically being formulated in conjunction with a co-thickener.

The class of medium thickening NiSAT’s are acting in between both other classes described above. As they are mainly affecting the mid shear range they are typically being formulated as general thickeners.

RHEOLATE[®] NiSAT grades are also in line with the latest requirements in terms of sustainability



Appendix

Test methods:

KU viscosity

KU describes the Krebs-Stormer viscosity; typically the mid-shear or appearing in-can viscosity is represented.

High-shear/ICI viscosity

Indicates the viscosity at high shear rates of 10000 s^{-1} measured by a cone/plate equipped ICI viscometer.

Rheology data

Determined using the Anton-Paar MCR 301 rheometer, equipped with PP 50 measuring geometry at a gap width of 1 mm, at a temperature of 23°C . In case of the oscillatory, amplitude sweep data shown an fixed angular frequency of 10 rad/s was pre-adjusted.

Brush-out levelling

25g of paint brushed out equally on leneta chart; levelling was evaluated relatively after 24 h drying time at room temperature; Measuring range: 0 = poor/5 = excellent; The larger the number, the better the result.

Roller/spattering resistance

40g of paint rolled on vertical wall (10 times up & down); Spatters collected on black chart underneath and judged visually; Measuring range: 0 = poor/5 = excellent; the larger the bar the better the result.

Salt spray testing

Salt spray resistance determined in accordance with DIN EN ISO 9227; Exposure time 500h.

Humidity resistance

Humidity test performed according to DIN EN ISO 6270-2; Exposure time 500h.

Overview graphics

Figure 1:

Combination of thickener classes

Figure 2

Schematic overview NiSAT structure

Figure 3

General overview available RHEOLATE® product classes

Figure 4

Schematic representation of network mechanism of NiSAT

Figure 5

Schematic representation of hydration shell

Figure 6

Schematic representation of controlled flocculation

Figure 7

Influence of hydrophilic/hydrophobic end groups on the product performance

Figure 8

Effect of various NiSAT types on rheology

Figure 9

Influence of on early water resistance

Figure 10

Influence of coalescents on NiSAT effectivity

Figure 11

Influence of on binder particle size

Figure 12

Influence of surfactants added via colorants

Figure 13

Influence of various HLB surfactants

Figure 14

Network disruption by surfactants

Figure 15

Newtonian NiSAT influence on the flow

Figure 16

Influence of Newtonian NiSAT on the viscoelasticity

Figure 17

Influence of Newtonian NiSAT on the brush-out levelling

Figure 18

Influence of Newtonian NiSAT on the roller/spatter tendency

Figure 19

Influence of pseudoplastic thickeners on flow characteristics

Figure 20

Influence of pseudoplastic thickeners on viscoelasticity

Figure 21

Influence of pseudoplastic thickeners on dripping

Figure 22

Influence of pseudoplastic thickeners on film resistance

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

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