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THICKER THAN WATER

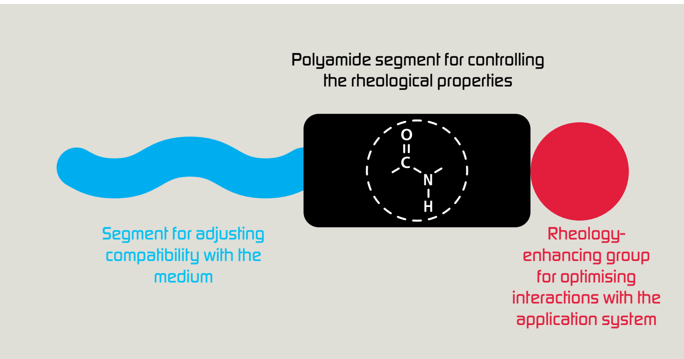
A new class of rheology additives for water-borne systems. By Dominika Bernert, Sylvia Bühne, Kathrin Möllers, and René Nagelsdiek, Byk-Chemie GmbH.

The market shift towards water-borne coating systems has made the adjustment of flow behaviour a core task. It has not yet proved possible to achieve this satisfactorily in all binder systems. New liquid rheology additives based on modified polyamides enable coatings manufacturers to meet a wide range of requirements that were previously the preserve of solvent-borne systems.

In almost all market segments, the shift towards water-borne coating systems continues unabated [1, 2, 3] and is increasingly affecting markets that were previously dominated by solvent-borne and solvent-free formulations. New water-borne alternatives need to have their flow behaviour adjusted because they can only be used successfully in the context of the rheological profile created for any given application. True, a large number of rheology additives are already available for water-borne systems. However, many of them suffer from major drawbacks, such as difficult incorporation, compatibility problems, dependence of the thickening behaviour on the pH, and the need for a time-consuming, cost-intensive activation process. Furthermore, the possible applications of different classes of rheology additive differ in respect of the best time and/or process step to incorporate them into the formulation. *Table 1* illustrates this for different classes of thickener.

Commercial liquid polyamide-based rheology additives have become firmly established in the area of solvent-borne coating systems in recent years. They support pseudoplastic flow and their easy handling opens up scope for post-addition*.

Figure 1: General structure of the new class of rheology additives.



* Liquid rheology additives based on polyamides should not be confused with diamides, which have long been available on the market as thickeners in the form of powders or pastes. The polyamide-based rheology additives are homogeneous, low-viscosity solutions of polymer chains with a block-like structure.

RESULTS AT A GLANCE

→ Polyamide technology, in the guise of rheology additives, for solvent-borne systems has been successfully adapted and optimised for use in water-borne systems.

→ The new additives are liquid, easy to handle, do not require any heat activation or involve a workaround via the production of pre-gels.

→ The rheology additives deliver good results in a large number of water-borne binder systems.

→ In water-borne epoxy formulations, the new additives exhibit pronounced tolerance towards hardener addition, i.e. there is no drop in viscosity after the hardener is incorporated.

→ The additives not only increase viscosity, but also control the viscoelastic properties of the coating and can therefore also be used to improve the orientation of effect pigments.

However, while liquid rheology additives within this product class have become established for use in solvent-borne, in high-solids and in solvent-free systems, the same cannot be said for water-borne formulations – until now.

A new class of liquid additives based on polyamide chemistry has been recently developed that can be used successfully to control the rheology of water-borne systems. This class of polymeric rheology additives is characterised by the structured composition of the molecule (*Figure 1*). Besides the polyamide segment, the polymer chain comprises a modification for adjusting compatibility in the water-borne coating system and one or more groups for optimising the rheological performance profile. The corresponding molecular segments can be adjusted to modularly adapt the additive for specific tasks and systems. Some examples of the corresponding areas of application are presented below.

Figure 2: Viscosity of a water-borne 2-pack epoxy formulation, before and after addition of the hardener to the formulation.

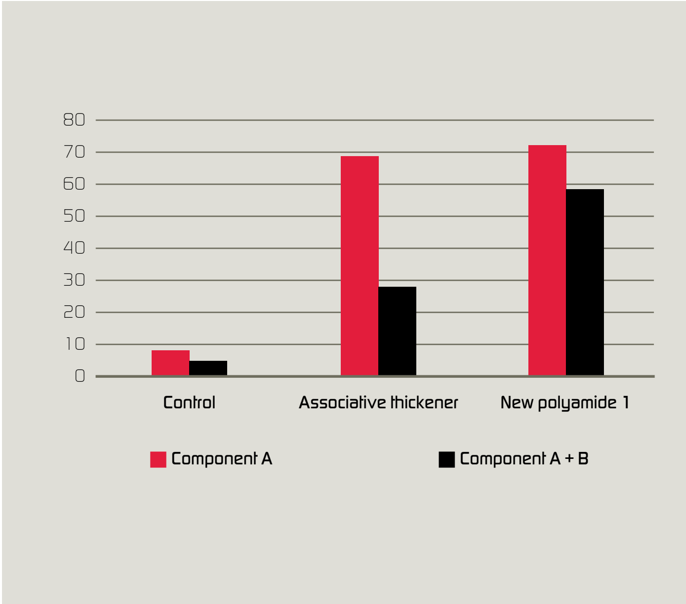
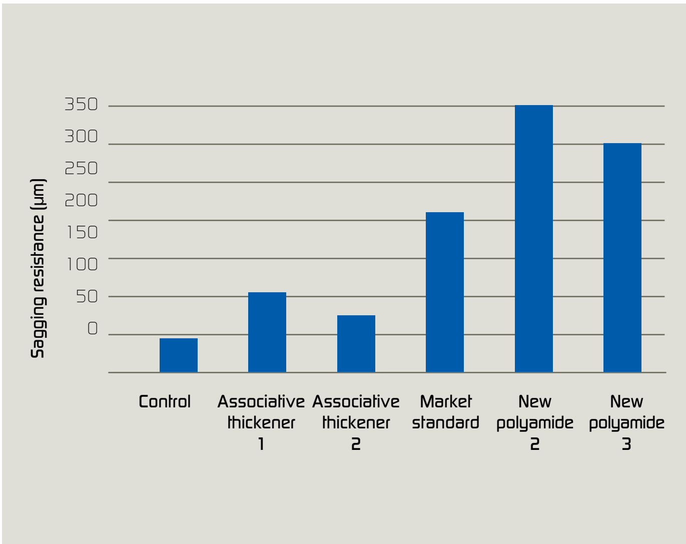


Figure 3: Sag resistance of a styrene acrylic clearcoat when different rheology additives are used (styrene acrylic clearcoat + 0.5 % active ingredient).



VISCOSITY CONTROL – AND MORE

The new class of rheology additives can be used in a wide range of binder systems. One example is water-borne epoxy coatings, which are becoming increasingly important in many areas of application. In protective coatings, especially, calls for environmentally sound water-borne solutions have recently been growing louder and louder [4, 5]. It is important that these systems have an adequate anti-settling effect for the particles (e.g. pigments, fillers) contained in the epoxy component and that the end products have the right non-sag properties.

Water-borne epoxy systems can be thickened with different classes of rheology additive, e.g. associative thickeners, acrylate thickeners, cellulose, and even phyllosilicates (hydroclays). However, some of these additives fail to either provide the desired flow behaviour, even after incorporation, or to exhibit sufficient storage stability in the epoxy component. Of those that do not exhibit these disadvantages, many experience a pronounced loss of effectiveness when the hardener is added. This sensitivity to hardener addition can be attributed to the interactions of the thickener with the hardener component itself or the formulation components present (e.g. surfactants).

Representatives of the new class of liquid polyamide rheology additives are characterised by strong shear-thinning and a marked tolerance to epoxy hardeners. As may be seen in *Figure 2*, when an associative thickener is used, the viscosity drops substantially after hardener addition. In contrast, with the new polyamide-based additive, no such substantial drop in viscosity is observed. Consequently, the associative thickener could be used as an anti-settling additive, but not for imparting sufficient sag resistance to the coating during application. The polyamide additive, on the other hand, meets both requirements and therefore represents a comprehensive solution for the system.

One particular area where high layer thickness is crucial is that of protective coatings, and the innovative polyamide-based rheology additives are ideal for such applications. A high layer thickness is the outcome not only of the actual viscosity value, however, but also of the type of flow and the viscoelastic behaviour. Rapid structural recovery and highly elastic properties have a positive effect on the non-sag properties of the applied coating. Whereas associative thickeners give

Figure 4: Oscillation measurement (3 ITT) for assessing anti-settling and non-sag properties in a 2-pack epoxy primer.

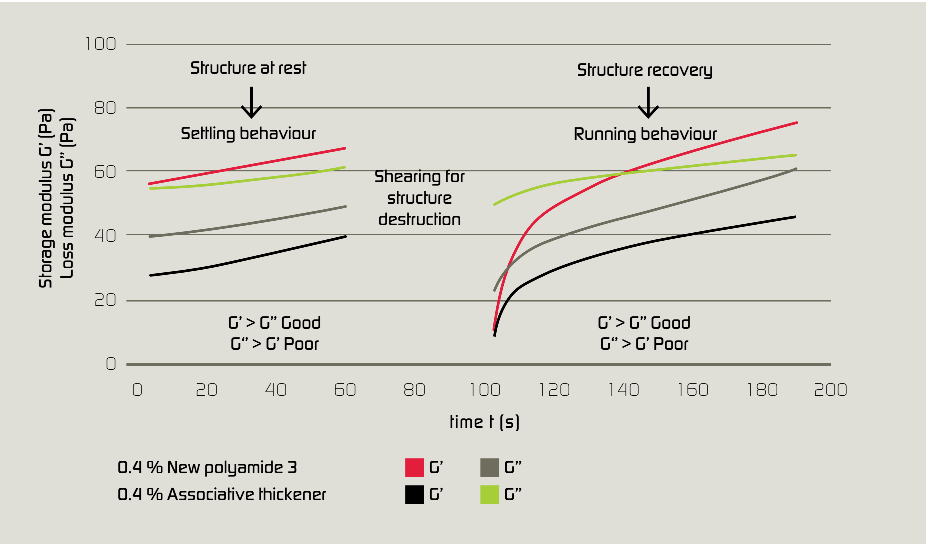


Figure 5: Anti-settling behaviour of a water-borne 2-pack polyurethane aluminium basecoat, without (left) and with (right) a polyamide additive (aluminium pigment: "Eckart Hydrolan IL 2154").

Table 1: The possible uses of selected classes of thickener.

Incorporation ... (	Into the millbase	After grinding	Post-addition
Associative thickeners (e.g. HEUR)	✔	✔	✔
Acrylic thickeners (ASE, HASE)	✔	✔	⊖
Layered silicates	✔	Only as pre-gel	⊗ (1)
Urea-urethane	⊖	✔	✔
Conventional amide pastes	✔	✔	⊗ (1)
New liquid polyamide additives	⊗ (2)	✔	✔

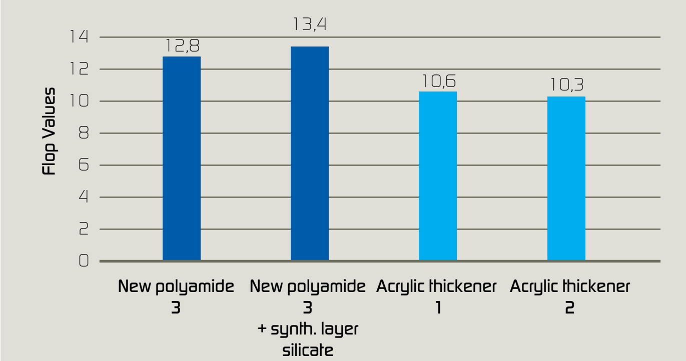
✔: Use recommended
⊖: Use with restrictions possible
⊗: Use not recommended
(1): The need for predilution has a significant effect on the overall composition of the system.
(2): Incorporation into the millbase leads to a risk of premature adsorption onto particle surfaces (e.g. in pigmented systems), i.e., the rheological effectiveness can be greatly impaired.

rise primarily to viscous flow in the formulation, the new polyamide-based rheology additives increase its elastic properties. Accordingly, as the example of the styrene acrylic clearcoat in *Figure 3* shows, the improvement in sag resistance is substantial compared with that of associative thickeners.

ANTI-SETTLING AND ANTI-FLOW PROPERTIES

The influence of the rheology additive on the viscoelastic behaviour of a water-borne coating can be observed by conducting oscillation measurements. The anti-settling performance and the anti-flow performance can be assessed in a three interval time test (3ITT). The first interval consists in measuring the structure initially at rest in oscillation mode. The second is a shearing interval in which the structure is destroyed before, in the third, structural recovery is re-assessed in oscillation mode (see *Figure 4*). In the presence of a commercial associative thickener, the water-borne epoxy system in both oscillation intervals exhibits a larger loss modulus (G'') than storage modulus (G'). In contrast, in the presence of new polyamide additive 3, the storage modulus (G') of the system is higher than the loss modulus (G'') in both oscillation intervals. The elastic properties predominate, while

Figure 6: Flop values in the 2-pack polyurethane system applied by pneumatic spray gun.



"The final application determines the optimal layer thickness."

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3 questions to Kathrin Möllers

When using the new rheology additives in protective coatings, what layer thicknesses do you recommend for achieving the best possible result? *Generally speaking, the final application determines the optimal layer thickness. In the protective coatings sector, a high layer thickness is traditionally required to achieve a good degree of protection against corrosion. Thanks to the new additive technology, achieving more than 500 µm in a single process is feasible.*

How well can the new polyamide-based rheology additives be integrated into existing systems? *They can be added to the let-down or post-added for viscosity adjustment in aqueous systems, making them highly versatile in terms of their application. This versatility is, however, reliant on the system containing a cosolvent. In particular, the use of alcohols is recommended.*

What are your next steps? *EP systems, especially aqueous systems, are extremely varied in terms of their composition and behaviour and therefore have different requirements. In the future, we will ensure that we can offer optimised solutions for all of these varied systems.*

the overall viscosity remains in a range comparable to that obtained with the associative thickener. Both the dominant elastic components in the undestroyed structure (at rest) and the rapid increase in elastic components during structural recovery show that good anti-settling and anti-flow properties can be achieved with the innovative polyamide-based rheology additives.

ORIENTATION OF EFFECT PIGMENTS

The modular structure of the new polyamide-based rheology additives also allows adjustments aimed at optimising the interaction with specific formulation ingredients. Hence, it is possible to use the products in a variety of systems other than epoxy coatings, such as 2-pack polyurethane systems. Due to their viscoelastic properties, the new class of rheology additive also demonstrates potential for use in the area of pigment orientation. Aluminium basecoats are an example of this. In these, a good rheology additive is expected to not only provide effective anti-settling, but also to deliver optimal orientation of effect pigments in the application (optimal flop). The significance of the viscoelastic properties, i.e. the viscosity and elasticity components, for the orientation of effect pigments in water-borne basecoat formulations has been explained elsewhere [6].
Figure 5 shows the much improved anti-setting behaviour of aluminium effect pigments, which was achieved in the presence of the new class of additive in a water-borne 2-pack polyurethane system. *Figure 6* shows the application result for the same coating system with regard to the orientation of effect pigments (flop). The attainable flop was greatly increased, compared with that of commercial acrylic thickeners, through the use of the new polyamide rheology additives. This effect was further optimised by combination with a synthetic phyllosilicate.
A new class of liquid polyamide-based paint additives for controlling the rheological behaviour of water-borne systems is now available. Unlike conventional thickeners, these polyamides do not require heat activation. They are provided as an easy-to-use, low-viscosity solution and do not require any extensive production of a pre-gel. The molecular structure of this additive class can be adapted to the intended use. A commercial solution is already available. It can be successfully used in water-borne epoxy coatings, as well as in other types of binder, to control flow behaviour.

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