Modified Ureas: An Interesting Opportunity to Control Rheology of Liquid Coatings

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Summary: Modified urea compounds can be used as very powerful liquid rheology additives in coatings. Their rheological impact in various coating systems is directly related to the specific chemical modifications that can be made to the polyurea molecule. Modifications evaluated were made using end groups of varying polarities such as low polarity alkyl groups, medium polarity segments, or highly polar structures. Analysis of rheological behavior in various types of coatings indicates the presence of two different thickening mechanisms (H-bonding between urea and urea groups of the additive, and the association of the additive with the binder). These additives result in coatings with exceptional resistance to settling during storage, along with good sag resistance. Some urea type additives used in combination with conventional rheology modifiers such as fumed silicas show synergistic effects. Advantages for coating producers and users will be shown using several practical application examples compared with conventional rheological additives.

Keywords: anti-settling, sag control, modified urea, paint additive, synergism, thixotropy, rheology additive

1. Modified urea rheology additives: chemistry and method of action

Modfied urea rheology additives are solutions of modified urea functionalities in the highly polar aprotic solvent N-methyl pyrrolidone (1-methyl-2-pyrrolidone). Their chemical structure is shown on Fig. 1. They can be produced by reacting monoalcohols with diisocyanates into monoadducts, which then can be reacted with diamines into diureas. Since the monoadducts still may contain traces of diisocyanates, besides the diureas also polyureas are formed in small amounts. However, the solubility properties of polyureas is worse that that of diureas, therefore the residual diisocyanate content of the monoadducts must be minimized in order to obtain the lowest possible levels of polyureas.

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Three modified urea modifications have been developed: one with low polarity end blocks, another one with medium polarity end blocks and a third with highly polar ones. Shown below in Fig. 2 are the most important technical and physical data:

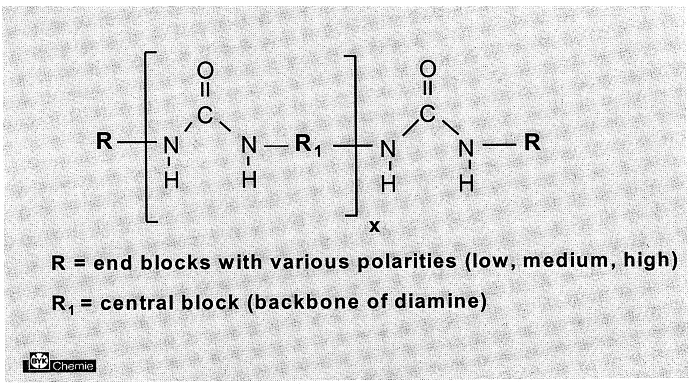

Figure 1.General structure of modified urea rheology additives

Figure 2. Modified urea thickeners

	R= Low polarity block	R= medium polarity block	R= highly polar block
Solvent	NMP (1-Methyl-2-pyrrolidone)	NMP (1-Methyl-2-pyrrolidone)	NMP (1-Methyl-2-pyrrolidone)
Solids (wt %)	Ca. 25	Ca. 52	Ca. 52
Density (g(cm3)	1,05	1,13	1,13
Visual appearance	Clear, low viscosity yellowish liquid	Clear, low viscosity yellowish liquid	Clear, low viscosity yellowish liquid
*Commercial name	BYK-411	BYK-410	BYK-420

When employed in binders, the active substance of these liquid rheology additives is selectively insoluble and separates out after incorporation — in a network of polyurea molecules in microcrystals, interacting via H-bonding with each other. The polyurea network demonstrates pronounced pseudoplastic properties, shear thinning and true thixotropy with an easily detectable yield point. The hydrogen-bonding structure is shown on Fig. 3.

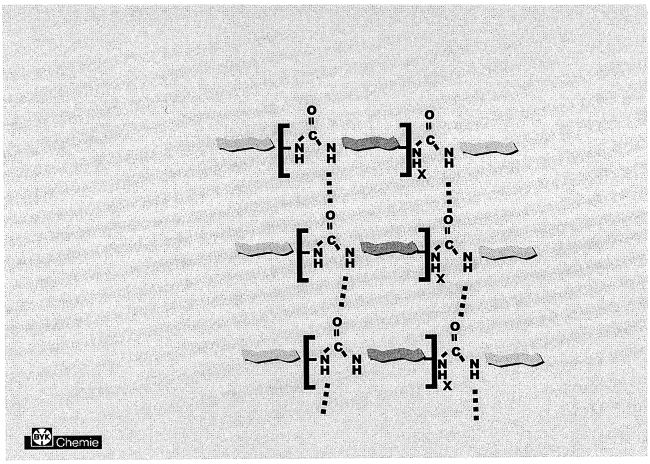

Figure 3. Hydrogen-bonding structure between modified urea molecules

Modified urea additives provide at lower shear rates a very strong viscosity increase, however, at elevated shear rates hardly any viscosity increase can be observed. This rheology is very favourable for most coating applications, since the pronounced increase of low shear viscosity improves the anti-settling behaviour as well as sag control characteristics, while the low viscosities at higher shear rates improve paint application properties. Low viscosities at higher shear rates also can help reduce solvent addition for spray applications, therefore the usage of polyurea additives fits very well within today's trends to formulate low-VOC systems.

The typical rheology behaviour of modified urea thickeners can be observed of Fig. 4, where the rheology of a high-solids long oil alkyd resin, modified with an organoclay, with hydrogenated castor oil and with the lower polarity modified urea thickener is displayed.

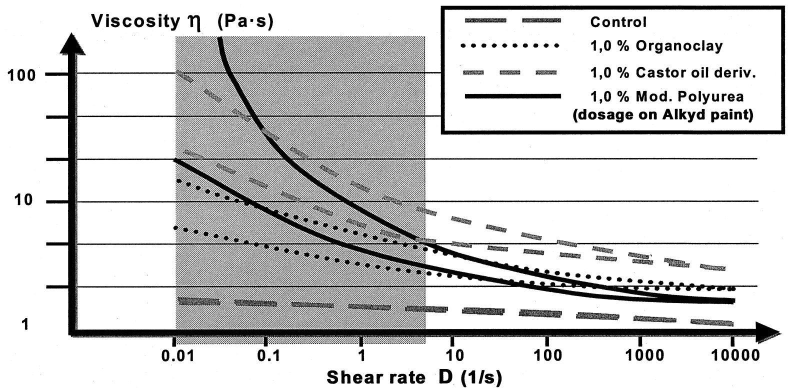

Figure 4. Viscosity characteristics of the modified urea thickener in comparison with organoclay and castor oil derivative

Additive level was in all cases 0.5 %. The very much different rheologies predict a stronger anti-settling and sag control behaviour with the modified urea thickener.

2. Rheology effects as function of modification

2.1 Characterization of modified ureas under various polarity conditions

It is very difficult to find a system, where all three modified urea componds can be characterized in a proper way. However, a suitable test system was found by using a thermoplastic acrylic resin which is soluble in aliphatic isoparaffinic solvents (Isopar H) and also in isopropyl alcohol. Resin solutions with 100, 75, 50, 25 and 0 % Isopar H and 0, 25, 50, 75 and 100 % isopropanol have been modified with each three modified urea compound. Viscosity measurements on these model systems display, that by using a higer polarity end group as modification, also the viscosity maxima of each product is shifted into the higher polarity domaine (Fig. 5).

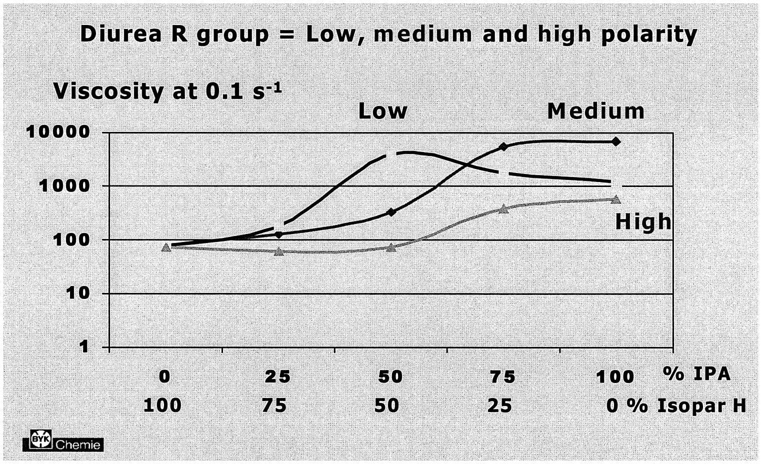

Figure 5. Influence of the system polarity on effectiveness of modified ureas with various polarities

However, in the case of the highly polar modification, the optimal polarity area can be reached only outside the range, when organic cosolven-water mixtures are used as solvent.

2.2 Low polarity urea thickener

The lower polarity new liquid thixotrope does not provide any remarkable thickening performance in pure solvents, but works well when binders – especially fatty acid modified ones – are employed. With increasing solids of the resin, modified with the urea thickener, the thickening effect will be exponentially improved [Fig.6].

The exponentially increasing sag control as function of resin solids content suggests that not only H-bonding interactions between polyurea molecules but also associative interactions with the resins may improve the rheology performance. Due to these pronounced associative interactions, the low polarity urea modification is ideal for higher solids applications but not for lower solids systems.

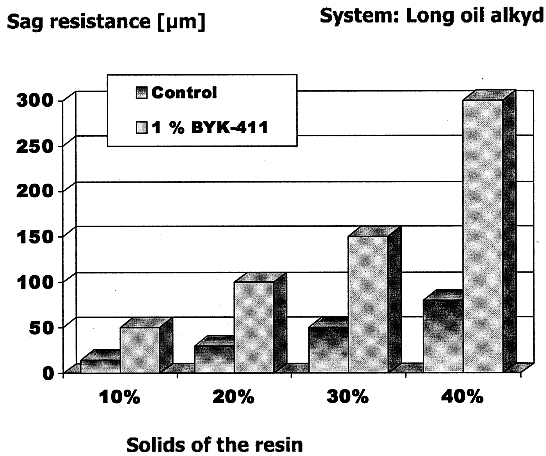

Figure 6. Sag resistance in a long oil alkyd paint, as a function of resin solids

According to lab test results, typical dosage levels of the non-polar modified urea thixotrope to improve anti-settling are 0.1-0.3 %. For sag control improvements, dosages above 0.3 % can be recommended.

2.3 Medium polarity urea thickener

This material builds up a thixotropic network in almost any kind of medium polarity solvents and solvent blends and works also in medium polarity resins or in their blends. The achieved rheology effect is almost independent from the binder content of the system. Just 2-3 % medium polarity polyurea thickener can "solidify" solvents such as xylene-butanol blends, resulting in gelly structures with a high yield point.

The best rheology performance can be achieved in typical medium polarity binders such as OH-functional polyurethanes, acrylic resins, polyesters, as well as in epoxies, vinyls, UV-binders, melamines and many other resins. Typical usege levels are 0.1-0.3 % for anti-settling, and 0.3-1 % for sag control.

2.4 Highly polar urea thickener

The high polarity urea modification provides best rheology effectiveness in aqueous formulations. Blends of water-soluble organic cosolvents with water can be modified with this additive, resulting in highly thixotropic properties. In heavily pigmented aqueous slurries and pigment concentrates – even without cosolvents – a very strong anti-settling effects can be achieved. Typical anti-settling effects of the highly polar urea modification are displayed on Fig. 7.

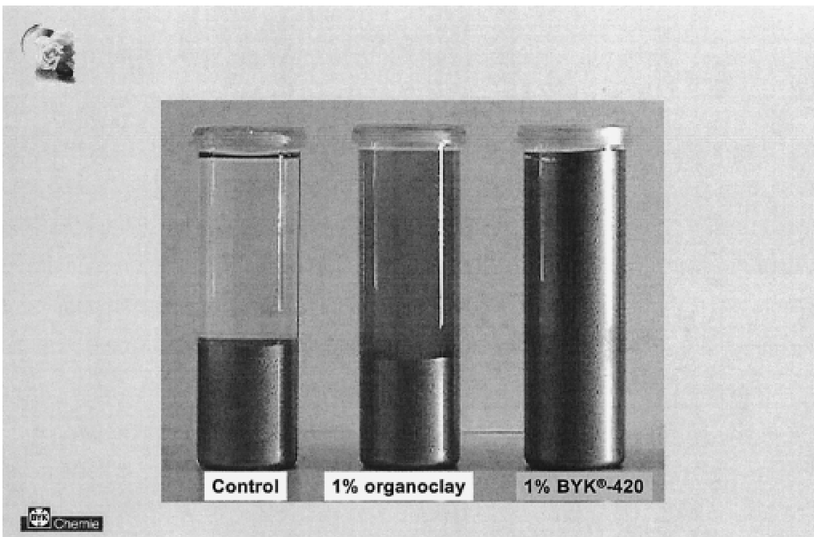

Figure 7. Anti-settling comparison between an organoclay and the high polarity modified urea in an aqueous pearlescent pigment slurry

3. Rheology Effects in Combinations with Other Rheology Additives

Since many other rheology additives also interact via H-bonding, it is also possible to combine the modified ureas with other rheology additives in order to achieve synergistic effects, and tailor-made rheology properties for certain applications. It has been found, that the medium polarity urea thickener shows very strong synergistic effects with fumed silicas, especially in solvent-free epoxy resin formulations. Thixotropy recovery properties can be optimized by using these combinations for maxium sag resistance in high-shear applications (airless spraying).

Thixotropy recovery properties by using fumed silica, modified medium polarity urea and combination of both in a solvent-free Bisphenol A-type liquid epoxy resin are displayed on Fig. 8. The viscosity improvement by using modified urea alone is better, than with fumed silica, but the network build-up after pre-shearing takes much longer time. In high-shear applications only the combinations of both additive, resulting in shorter recovery times and high viscosities, perform well for sag resistance.

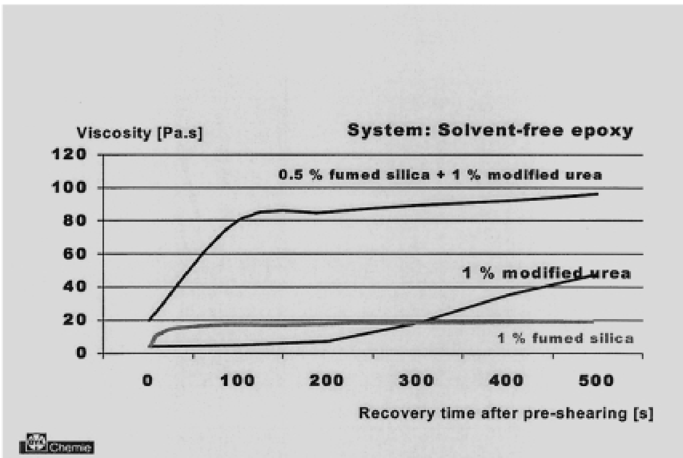

Figure 8. Thixotropy recovery after pre-shearing, measured as viscosity at 0.1 s-1 shear rate with modified urea, fumed silica and combination thereof

4. Incorporation

One of the greatest technical advantages of the modified urea additive chemistry is the fact that optimal rheology improvements (sag resistance, anti-settling) can be achieved just by post-addition to the finished paint. Neither grinding, nor heat activation or pre-gelling are necessary to achieve the best rheological performance.

The method of additive incorporation is also important. For optimal effectiveness and for homogeneous gel structure, a rapid and homogeneous incorporation of the additive is desirable, avoiding too high shear forces like pigment grinding conditions. Optimal is when using typical letdown conditions as used in the paint industry. An incorporation into the millbase is recommendable only if good anti-settling but no sag control is the target.

To test rheology properties, it is recommended to wait until the final viscosity build-up is completed, usually overnight.

5. Applications

The modified urea based liquid thixotropes can be recommended to improve anti-settling and sag control properties for a very wide range of applications.

The lower polarity modification is more often used in long and medium oil alkyd resin based systems, dissolved in mineral spirits. Applications include architectural coatings, marine coatings and also heavy-duty systems – almost everywhere where low polarity alkyd resins can be used. Applications in primers, under coats and topcoats are also possible.

The medium polarity version is successful in almost any type of medium polarity systems from coil coatings, wood coatings through general industrial coatings and automotive systems up to the protective and marine coating applications. In automotive base coats, special advantages can be achieved through the relatively slow thixotropy recovery of the polyurea network which can provide excellent anti-settling as well as very good metallic flake orientation and good levelling at the same time. Applications in printing inks and PVC plastisols also exist.

The high polarity modifications is mainly used as anti-settlig additive in aqueous pigment slurries and in pigment concentrates for architectural and industrial coating applications, also includung high quality systems such as automotive basecoats.

6. Advantages over conventional thixotropes

Compared to the commonly used rheology control additives, the new technology offers some unique advantages. The main advantage resides in the liquid form of the additive, which makes it much easier to handle. When replacing hydrogenated castor oil or polyamide modified thickeners by polyurea, other primary advantages are no requirement of heat activation for incorporation and the much lower heat sensitivity on application. Compared to organoclays and fumed silicas, the major advantage is the lower dosage and the very little or no influence on gloss. In certain cases, combinations of modified urea thixotropes with fumed silicas result in very strong synergistic effects (Fig.8).

7. Conclusion

Liquid rheology additives based on modified urea functionalities have been developed to solve settling problems and to improve sag control properties. Modifications for low polarity higher solids solventborne and solvent-free systems (typically alkyd resins), further for medium polarity low to high solids and solvent-free systems and for aqueous systems do exist, and provide unique advantages for the coatings formulators.