Temperature-stable viscosity behaviour

The rheological demands placed on automotive coatings are severe. A new class of rheology modifier known as PMPU (Polyether-Modified Polymeric Urea) provides the required fast pseudoplastic recovery of structure after spraying, as well as high temperature stability to prevent sagging during cure. A combination with a polyamide thickener can optimise performance.

New pseudoplastic thickener effectively limits sag during drying
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In the automotive industry, the demands placed on paint properties are very high and are constantly increasing. Not only must the paints have a high degree of chemical and mechanical resistance, but they must also be quick to process.

For this reason, automotive OEM coatings make use of acrylic/melamine or polyester/melamine-based stoving systems as well as forced drying 2K PU systems. These systems are also used for automotive refinishing and for plastic and industrial coatings.

Particularly high demands are placed on topcoats and clearcoats, since they are crucial to the overall impression of the paintwork. In this case, in addition to the gloss, great importance is placed on the sagging and levelling characteristics.

The paint must be free of teardrops at the required film thickness even on vertical surfaces while at the same time it must provide the best possible levelling properties to provide the ideal visual impression. Rheology additives or rheologically modified resins are indispensable tools for improving sagging behaviour. They have to fulfil high requirements for all processing operations, from adjusting the viscosity to application and drying.

Demands for higher film thicknesses and some changes to application conditions run contrary to levelling requirements. It is therefore important to achieve an ideal balance between sagging and levelling behaviour during application.

Main rheological requirements in automotive systems
For liquid paints, a flow cup is used to adjust the spraying viscosity. To ensure effective processability, the rheological additive should have pseudoplastic flow behaviour, since the time-dependency of thixotropic flow behaviour makes the flow time considerably more difficult to adjust. If the paints have a gel-like structure when undisturbed, higher solvent quantities are frequently added, which has an adverse effect on the solids and thus on the film thickness. Depending on the end use, pneumatic or bell spray equipment is used to apply the coatings, subjecting the paint to very strong shear forces. The rheological additive must therefore be shear-stable on the one hand, but on the other hand a pseudoplastic flow behaviour is once again needed, since it must be possible for the viscosity to rise as quickly as possible after application.

In addition to increasing the viscosity after application, strongly elastic properties (viscoelasticity) also have a positive effect in preventing sagging. Achieving the right balance between sagging and levelling behaviour is very important in this case, since too fast a recovery of structure has a negative effect on levelling.

During the evaporation and drying periods, the paints are subjected to highly variable temperatures. The temperature during the evaporation period may range from room temperature up to 80 °C. The actual drying process also has a wide temperature range between 50 °C and 140 °C, depending on whether a forced drying system or a stoving system is used.

Until crosslinking occurs, the paint remains liquid and can therefore sag. The rheological additive must maintain a temperature-stable viscosity behaviour so that the sagging behaviour achieved during application does not deteriorate due to the increasing temperatures during the evaporation and drying periods.

In the finished coating, the effects of the additive on appearance properties such as UV and temperature resistance, and the effect on gloss and haze are also important for the suitability of the product. Good compatibility of the additive is essential to achieve high gloss and low haze in the coating.

Main types of rheology modifiers
Typical rheology modifiers, which are used to improve the sagging behaviour of solventborne vehicle topcoats (both clearcoats and pigmented coatings), include hydrophobically-modified fumed silica and organoclayes, in addition to rheology-modified resins (RM resins), known as sag control agents (SCAs) in the industry.

Not only is the powder form of fumed silica and organoclayes a disadvantage, but so are the shear forces they require for dispersion/activation. If the dispersion is insufficient there is a risk of seeding. Further disadvantages for clearcoats are the tendency towards turbidity in the liquid coating, and adverse effects on gloss and haze in the final coating.

Sag control agents have a limited range of use. Since they are resins, they make the choice of raw materials less flexible, and post-correction of sagging behaviour is not possible. In addition, they are usually highly turbid in their delivery form which is why they are not used in automotive refinishes.

Other typical rheology additives based on polyamides or castor oil derivatives are not used for these types of applications, because they are difficult to work with and their viscosity behaviour does not offer the required temperature stability.

New chemistry offers high-temperature stability
PMPU, an abbreviation for Polyether-Modified Polymeric Urea, is a new class of rheology additive. It is an easy-to-use liquid rheology additive, since it can be incorporated by
stirring it in at the end of the coating production process. It provides excellent compatibility and is therefore particularly suitable for clearcoats, since it also does not cause any turbidity in liquid paints (Figure 1).

Urea-based liquid rheology additives have long been known in the market as so-called “liquid thixotropes”. PMPU is characterized by a significantly higher molecular weight, a stronger pseudoplastic flow behaviour and good shear stability. In addition, the product ensures temperature-stable viscosity behaviour over the entire processing range of 20 °C to 140 °C (Figure 2). This graph shows a direct comparison of the viscosity behind of a single-pack clearcoat which was modified with different rheology additives or a rheology-modified resin to the coating without additive (control).

Application-specific evaluations
An application-specific evaluation of the sagging and levelling behaviour was conducted in different coating systems based on solvent-borne single-pack polyester and acrylic/melamine systems as well as in 2K polyester/isocyanate or acrylic/isocyanate systems.

Prior to application, the spraying viscosity of the liquid paints was adjusted using flow cups. Either pneumatic or bell spray application was used, depending on the application, and paint was applied to a vertical perforated steel panel with the thickness varying in a wedge pattern. Both application and drying processes were carried out on the panel in a vertical position. After drying, the film thicknesses of the dry coating areas showing no teardrops were measured (Table 1).

The effect on levelling, gloss and haze was evaluated on separate levelling panels with a constant film thickness (Table 2). Levelling was measured in terms of the distinctness of image gloss (DOI) in the final coating.

Using PMPU resulted in a significant improvement in the sagging behaviour of all test systems compared to the control. In the 1K stoving system, improved sagging behaviour was also achieved compared to the standard in both test systems with 1 % of the active substance. Another advantage was the reduced effect on turbidity in the liquid clearcoat. In the 2K clearcoat, the sagging behaviour improved with just 0.7 % active substance of PMPU compared to the standard; the DOI levelling was hardly changed.

Some principles of rheological measurement
The rate of structure recovery is an important factor for improving sagging behaviour when using the rheological additive. During the evaporation period and at the beginning of the drying period when the temperature increases, the coating can sag so long as it is still liquid. The structure recovery of a coating can be demonstrated by oscillation measurement using a rheometer, since the viscoelastic behaviour of a sample changes due to structure recovery. Viscoelasticity is a combination of elastic and viscous properties.

While elastic substances store deformation energy when under shear load and release this energy once the load is removed (eg, spring: 100 % elastic), viscous substances convert this energy into frictional heat during the flow process (eg, water: 100 % viscous).

For the oscillation measurement, the sample was measured non-destructively so that the structure could recover after shearing during application. The measurement provides the rheological values $G'$ (storage modulus = elastic part) and $G''$ (loss modulus = viscous part) [1].

The storage modulus $G'$ was observed as a proportion of the structure recovery, since the increase in $G'$ can be equated within the recovery of the sample structure. The higher the measured value for $G'$, the stronger is that part of the structure of the sample that prevents sagging.

Effects of temperature on rheology compared
To simulate structure recovery after application, a measurement profile was created, making it possible to evaluate the effectiveness of the rheology additives during the evaporation period and at the beginning of the drying period.

For this measurement, three samples of a 1K stoving system were applied by bell spray application. The liquid paint layers were then scraped off the panel and used for measuring. The initial part of the measurement was carried out at room temperature. The second part of the measurement used a temperature ramp ranging from 20 °C to 60 °C. The frequency and deformation parameters were kept constant (Figure 3).

In addition to the PMPU, the paint was measured without any rheological additive (control) and in direct comparison to a polyamide, since this class of additive is known to have a strongly temperature-dependent viscosity behaviour.

The first measurement showed the structure recovery after shearing and therefore started at a low level. During the first 200 seconds, the structure recovery at room temperature occurred at various speeds, depending on the rheology additive used. The control, which contained no rheology additive, showed no change in $G'$ over the entire measuring range, meaning that there was no recovery of structure. The polyamide showed excellent structure recovery in the first part of the measurement (evaporation period at room temperature). However, the temperature stability of the rheology effect was poor. The structure degraded significantly during the second part of the measurement as the temperature increased, and it even dropped down to the control level during the measurement.

For the PMPU, a significant structural recovery was visible in the first part of the measurement too. During the second part of the measurement, however, it behaved quite differently from the polyamide, the increase in $G'$ being clearly greater the higher the temperature, thus improving structural recovery. A faster recovery at higher temperatures prevented the paint from sagging at the beginning of the stoving period.

Combined additives optimise performance
During the PMPU development period, application tests by both pneumatic spraying and bell were carried out for automotive OEM coating. The shear forces were extremely high for the bell application method, placing high demands on the structure recovery of the rheological additive. As can easily be seen in Figure 3, the polyamide showed a stronger structure recovery than the PMPU immediately after application during the evaporation period, but lost its effectiveness during the stoving period, whereas this is where the PMPU showed its strengths.

Due to this very different behaviour, the question was whether a combination of these products could provide advantages in relation to the sagging and levelling behaviour. In the following series of tests, the combination...
of the two distinct types of additive PMPU and polyamide was therefore also used in different stoving systems and forced drying coatings, and applied by bell spray application.

An acrylic/melamine-based 1K stoving system is shown here as an example (Table 3). For the comparison, the additives were tested alone as well as in combination against a standard and the control. PMPU and polyamide were used in combination in different mixing ratios. The comparison was based on the use of the same total quantity of active substance for each additive.

The application results showed an improvement in the sagging behaviour for the PMPU alone compared to the control; however, the improvement using 1 % of the active substance was not as good as with the standard material tested (RM resin).

The polyamide showed almost no improvement in the sagging behaviour when used alone, and it even had a negative effect on gloss and haze.

In contrast, the combination of PMPU and polyamide showed a significantly better sagging behaviour than the market standard. Performance depended on the mixing ratio: as the ratio of polyamide increased, the sag resistance decreased.

A 70:30 mixing ratio of PMPU to polyamide produced the best sagging behaviour and good gloss and haze values. The combination of the two classes of additive therefore allows specific control of the levelling and sagging behaviour by varying the dosage and mixture ratio. Due to their different chemistry, both additives have to be added separately. PMPU should be added first.

An effective additive for high-temperature curing

PMPU is a new class of rheology additive that ensures good application reliability through its temperature-stable viscosity behaviour, good structure recovery and shear stability. The product is ideal for coating systems applied with low viscosity and moderate film thickness (30 to 70 µm dry film thickness) and dried at higher temperatures.

In addition to clearcoats, its areas of application include topcoats and primers for automotive, plastic and industrial coatings. Moreover, PMPU can also be used to improve settling behaviour, particularly at higher storage temperatures. Its main advantages may be summarised as follows:

- Temperature-stable viscosity behaviour, fast structure recovery and shear stability ensure good application reliability.
- The excellent compatibility reduces effects on turbidity in liquid clearcoats and gives paint films a good appearance.
- The liquid supply form is easy to work with and can therefore be used for post-correction of sagging behaviour even shortly before application.
- Combined with a polyamide, specific control of the levelling and sagging behaviour is provided by varying the dosage and mixing ratio.

REFERENCE


Results at a glance

The rheological demands placed on automotive coatings, and especially OEM coatings cured at moderate to high temperatures, are severe. Application takes place under high shear, and a fast (pseudoplastic) recovery of structure is essential to prevent sagging. At the same time, any additives used must not prevent the achievement of a smooth glossy finish nor interfere with physical and chemical resistance properties. A new class of rheology modifiers known as PMPU (Polyether-Modified Polymeric Urea) is shown to offer the required fast recovery after spraying combined with high temperature stability to prevent sagging during cure. Optimum results may be obtained by a combination of temperature-stable PMPU with a polyamide thickener, which is very effective initially but loses its efficiency as the temperature rises.

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Figure 1: PMPU does not cause turbidity in a liquid clearcoat
Figure 2: Temperature-stable viscosity behaviour of PMPU
Figure 3: Dependence of structure recovery on time and temperature for polyamide and PMPU thickeners shows strong differences.
Figure from Temperature-stable viscosity behaviour

Table 1: Sagging behaviour and turbidity of two single-pack clearcoats

<table>
<thead>
<tr>
<th>Systems (acrylic/melamine)</th>
<th>Additive (active substance) on total post-addition</th>
<th>Turbidity, visual</th>
<th>Sag resistance, μm (dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control</td>
<td>Clear</td>
<td>24</td>
</tr>
<tr>
<td>System 1</td>
<td>RM resin (standard)</td>
<td>Strong</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>1 % PMPU</td>
<td>Clear</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>Clear</td>
<td>28</td>
</tr>
<tr>
<td>System 2</td>
<td>RM resin (standard)</td>
<td>Strong</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>1 % PMPU</td>
<td>Clear</td>
<td>38</td>
</tr>
</tbody>
</table>

Table 2: Levelling and sagging behaviour of 2K clear coat, taking distinctness of image (DOI) as an indication of levelling

<table>
<thead>
<tr>
<th>Additive (active substance) on total post-addition</th>
<th>Sag resistance, μm (dry)</th>
<th>Levelling (DOI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>36</td>
<td>94.0</td>
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<tr>
<td>RM resin (standard)</td>
<td>41</td>
<td>93.1</td>
</tr>
<tr>
<td>0.5 % PMPU</td>
<td>39</td>
<td>93.6</td>
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<tr>
<td>0.7 % PMPU</td>
<td>45</td>
<td>93.2</td>
</tr>
<tr>
<td>1.0 % PMPU</td>
<td>55</td>
<td>90.9</td>
</tr>
<tr>
<td>Additive (active substance) on total post-addition</td>
<td>Sag resistance, μm (dry)</td>
<td>Gloss 20°</td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td>--------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Control</td>
<td>16</td>
<td>84</td>
</tr>
<tr>
<td>RM resin (standard)</td>
<td>28</td>
<td>87</td>
</tr>
<tr>
<td>1 % polyamide</td>
<td>17</td>
<td>74</td>
</tr>
<tr>
<td>1 % PMPU</td>
<td>25</td>
<td>84</td>
</tr>
<tr>
<td>1 % PMPU/polyamide, 70:30</td>
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</tr>
<tr>
<td>1 % PMPU/polyamide, 50:50</td>
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<td>87</td>
</tr>
<tr>
<td>1 % PMPU/polyamide, 30:70</td>
<td>27</td>
<td>83</td>
</tr>
</tbody>
</table>

Table 3: Effect of PMPU/polyamide combinations in the single-pack clearcoat

Figure from Temperature-stable viscosity behaviour