1. Introduction

Acrylic thickeners are widely used in many different areas such as joint compounds, wood stains, putties, decorative paints, adhesives and sealants, industrial coatings. They are known to be very cost effective and easy to use in comparison with other thickening technologies.

Acrylic thickeners are particularly well adapted to provide very high viscosities at low shear rates. The effect is to impart to formulations a strong in-can structure with a good shear thinning behavior. Such characteristics provide benefits across a broad range of application, going from low to high solids water based formulations.

High viscosities at low shear rates help avoid sedimentation, sag, and improve tool load. Low viscosities at high shear rates help get an easy application, particularly for formulation with a high solids content.

Many acrylic thickeners are able to provide a pseudo plastic type rheology behavior. When going more in detail one would discover that pseudo plasticity is a very generic notion possibly covering a lot of nuances, thus differentiated application properties. The latter can be highlighted with water based systems such as gels, low solids formulations such as wood stains, or high solids formulations such as matt paints or plasters. For each type of formulation, the way to monitor the application properties imparted by different acrylic thickeners will be different. Monitoring can be about sedimentation, drip or crushing resistance, all specifically related to the rheology provided, or color acceptance, not directly related to rheology but to be considered as one of the most important side properties for paints.
1. Gel application example: sedimentation resistance

The pseudo plastic character is generally assessed by carrying out Brookfield viscosity measurement. Most formulators would expect that once the Brookfield viscosity is adjusted at a given value, properties such as sedimentation resistance would be set at the same level. Making the experiment shows that the reality is quite different. It can be done using three pseudo plastic type thickeners belonging to the Coatex range and making gels. Viscosities of the gels are adjusted in order to achieve a 100 rpm Brookfield viscosity of 2500 mPa.s. A dosage of 0.6% (active) of each the three Coatex thickener is required to get the same viscosity for the gels. The sedimentation resistance provided by gels can be checked by placing each made with a different pseudo plastic type thickener in 100 ml burettes. Small iron beads having the same size and weight are dropped simultaneously from the top of the burettes. The beads tend to drop down the gel. The time needed to reach the bottom of the burettes is measured, which corresponds to a sedimentation resistance measurement.

Measurement of the drop time highlights huge differences. About 8 seconds only are needed for the bead to reach the bottom when the associative thickener Rheotech 4800 is used. The expected working mechanism of Rheotech 4800 is based on gel forming with water and on hydrophobic interactions with other hydrophobic ingredients of the formulation. Since there are no other hydrophobic ingredients in a gel, the hydrophobic end groups of the thickener tend to self-associated into kinds of micelles. In that case, the mechanism is not very effective due to hydrophobic end groups which are not adapted.

The situation is slightly better when using Viscoatex 730. The working mechanism of Viscoatex 730 is based on the gel forming only, and therefore, it is well adapted for making strong and viscous gels. The iron bead needs a little more than 6 minutes to reach the bottom of the burette with is already a significant improvement against the previous case.
The gel ensuring the best resistance against sedimentation is the one made using Thixol 53L as the thickener. The working mechanism of Thixol 53L is very specific. Like other acrylic type thickeners, it turns water into a gel by reducing the mobility of water molecules thanks to hydrogen bounds forming between water molecules and anionic groups coming from the neutralized carboxylic functions. Its design allows reinforcing its effectiveness at very low shear rates by forming a hydrophobic network. The network is generated by specific hydrophobic end groups which are grafted on the principal polymer backbone and are particularly adapted to self-associate into micelles. As a result, very low shear rate viscosities increase within a few hours as the network is progressively forming. This exclusive working mechanism allows slowing down the iron bead drop. It reaches the bottom of the burette after 2 hours and 26 minutes.

The huge difference in terms of sedimentation resistance, as evaluated by the iron bead drop experience, can be correlated with viscosities values when they are measured at very low shear rates. Brookfield viscosities measurements correspond to shear rates between 0.1 and 20 s\(^{-1}\) but even 0.1 s\(^{-1}\) is not low enough to correlate with the sedimentation resistance tendency. Flow curves starting from much lower shear rates must be carried out to have better chances for a good correlation. Flow curves starting from lower than 10\(^{-4}\) s\(^{-1}\) can be obtained when using the latest generation of rotational rheometers. Flow curves corresponding to the gels show that viscosities values for shear rates between 10\(^{-6}\) and 10\(^{-2}\) s\(^{-1}\) differ by several magnitudes depending on the thickener used, which can be easily correlated with the drop time of the iron beads. The higher the viscosities at very low shear rates, the better the sedimentation resistance.

Measured at very low shear rates, viscosities a little bit less than 10\(^5\) mPa.s can be associated with a drop time of 6 seconds, 10\(^6\) mPa.s with a drop time of about 7 minutes and 5.10\(^7\) mPa.s with a drop time of about 2 hours and 26 minutes. The correlation becomes extremely clear when using log scales for both viscosities and drop time axis.
Pseudo plastic thickeners are needed as soon as anti-sedimentation properties have to be achieved, but some choice has still to be done to get the best effectiveness in that area. Such thickeners are also adapted to adjust the in-can appearance as well as the tool load (on a brush, a roller or a spatula). In-can structure can be tuned from flowing to gel-like structures depending on the thickener selected

2. Wood stain application example: drip resistance

The dripping tendency can be evaluated as a function of the thickener used. To fully understand the importance of a complete rheology profile, it is important to start the comparison with formulations whose Brookfield viscosities are adjusted initially to a given value. The 10 rpm Brookfield viscosity of the wood stains studied here is each time adjusted at about 12500 mPa.s using each of the three pseudo plastic type thickeners already used before. Both the resulting in-can texture and dripping tendency are monitored.

The wood stain is based on 56% of acrylic binder and is tinted using blue and green colorants. Brookfield viscosity is adjusted using from 0.4 to 0.5% of active thickener. Stormer viscosities obtained using Rheotech 4800 are higher than with the two other thickeners tested. Stormer viscosity is generally related to a given feel at hand stirring. The higher the Stormer viscosity value, the better the perceived quality at hand stirring.

The dripping tendency cannot be anticipated from the perceived quality at hand stirring. The best drip resistance is achieved using Thixol 53L which imparts the lowest Stormer viscosity. The worst is obtained with Rheotech 4800 giving the highest one. Once again, adjusted Brookfield viscosities or higher Stormer viscosity give no guarantee for achieving a given anti-drip effect.
The correlation with anti-drip effect is to be found again in viscosities obtained at very low shear rates. Complete rheological curves carried out on the different wood stains reveal that viscosities become higher starting from 0.1 s\(^{-1}\) down to 10\(^{-4}\) s\(^{-1}\) when Thixol 53L is used. The same curves show that viscosities are higher starting from 2 s\(^{-1}\) and higher when using Rheotech 4800. It can be correlated with a better in-can appearance coming from a cream-like structure.

The anti-drip effect can also be correlated with the viscoelastic character of the formulations. Following the evolution and the phase angle shift as a function of shear stress is of particular interest. The positioning of the phase angle shift at low shear stress is a good indication of the anti-drip tendency. The lower the positioning of the resulting elastic plateau in terms of angle value, the higher the potential against drip. The elastic plateau is situated at 37° when using Thixol 53L giving the best drip resistance and at 52° when using Rheotech 4800 giving the highest flow and the lesser drip resistance.

3. Matt paints application example: color acceptance

The main function of thickeners is to provide a given rheological profile to water based formulations. It was shown that drip resistance can be tuned by adjusting viscosities measured at very low shear rates or trying the get the elastic plateau situated as low as possible in terms of phase angle shift. On the other hand, the perceived quality at hand stirring can be tuned by adjusting the Stormer viscosity to higher values. Pseudo plastic type thickeners may also have an impact on various side properties such as optical properties, storage stability or color acceptance.
Color acceptance is checked by adding 5% of black colorant to a matt paint. The 10 rpm Brookfield viscosity is adjusted by adding the needed dosage of each of the three tested thickeners, Thixol 53L, Viscoatex 730 and Rheotech 4800 in order to achieve a 10 rpm Brookfield viscosity of about 25000 mPa.s. The black colorant is known to be a good revealer of the color acceptance level.

Drawdowns of the tinted matt paints enable to measure the color strength. Rub-out out tests are carried out on fresh applied tinted matt paints to determine whether the pigments are dispersed and stabilized well enough to stand different levels of shear stress as the ones exerted on paints surface by the finger rubbing. The color acceptance is said to be good if there is no noticeable color difference between the rubbed and the non-rubbed areas. Results show that Rheotech 4800 provides the best color acceptance, followed by Thixol 53L and Viscoatex 730. The difference between Rheotech 4800 and Viscoatex 730 is very noticeable.

4. **Plaster application example: crushing resistance**

Applications tests related to the rheological behavior can be very different depending of the type of formulation. The one used to evaluate plasters is very specific. Plasters principally consist of very small amount of binder and high load in coarse fillers. Therefore the amount of thickener to add in generally quite low (0.22% of active thickener in our example).

The application test for plaster or putties is a crushing test. Indeed, a given resistance under the trowel or the spatula is required during the application to get the given and even thickness needed. The crushing resistance is determined by putting a small amount of plaster (2 grams) between two glass plates and by adding a 2 kg weight on the glass plate to exert the needed
pressure (or shear stress). The diameter of the crushed plaster between the two glass plates is measured as the result.

The plaster applicators need to feel a given resistance under their trowel or spatula. A higher resistance results in a smaller diameter when carrying out the specific test. The smaller diameter is obtained using Viscoatex 730 as the thickener. Brookfield viscosities carried at 1 rpm show that Viscoatex 730 is imparting the highest values (1'750'000 mPa.s), followed by Rheotech 4800 (1'250'000 mPa.s) and Thixol 53L (500'000 mPa.s). Considering the diameter measured in each case, the level of correlation with 1-rpm Brookfield viscosity values seems quite good.

Having evaluated three Coatex pseudo plastic type thickeners, one cannot rule that one is better than the others. Each would impart specific responses to specific needs related to different types of formulations. Thixol 53L provides a unique thixotropic effect along with a high sedimentation and drip resistance.

Rheotech 4800 imparts an excellent color acceptance and a creamy appearance to most formulations thus a higher perceived quality. Viscoatex 730 contributes to achieve a high crushing resistance for plasters and putties.
5. **New product for Brazilian putty formulations**

There are basically two different formulations of putty in Brazil, one of them for indoor use only (Massa Corrida) and another for outdoor use (Massa Acrílica), which is also applied on damp places such as walls in the edge of bathrooms or kitchens. Once indoor putty represents most of the market share it was used its ordinary formulation to perform the comparative thickeners evaluation.

Samples of indoor putty were thickened with three Coatex pseudo plastic thickeners as well as Market samples thereafter crush test and low-shear viscosity measurements were done. Brookfield viscosity carried at different speeds (1, 10 and 100 rpm) and results show that Rheotech™ 4800 is imparting the highest values followed by Massa 02 and Viscoatex 730 among Coatex portfolio.

Evaluating Market products, Sample 3 show high viscosity then after Sample 2 and Sample 1. However, as the smaller diameter of the sample in the crush test represents the better thickening power, Rheotech™ Massa 02 as well as Sample 1 thickener show the best results.
Applications tests related to water absorption and abrasion resistance are carried out according Brazilian Standard - NBR 15303 and NBR 15312.

Evaluating pseudo plastic type thickeners all of them provide results of water absorption and abrasion resistance according requirement Brazilian regulations.

Absorption results tests show outstanding performance and above required by standard.
6. Conclusion

Pseudo plastic type thickeners are needed to adjust various properties of water based formulations. Resistance against sedimentation, dripping and crushing are among the most typical ones. Tuning the in-can appearance, the tool load or the workability are other aspects that can be addressed. One should not forget other types of properties not directly related to rheology such as color acceptance. Some pseudo plastic type thickener are providing much better results than others in those areas. For all these reasons, pseudo plastic thickeners should be considered among the most powerful tools for anyone with the desire to improve its formulations.