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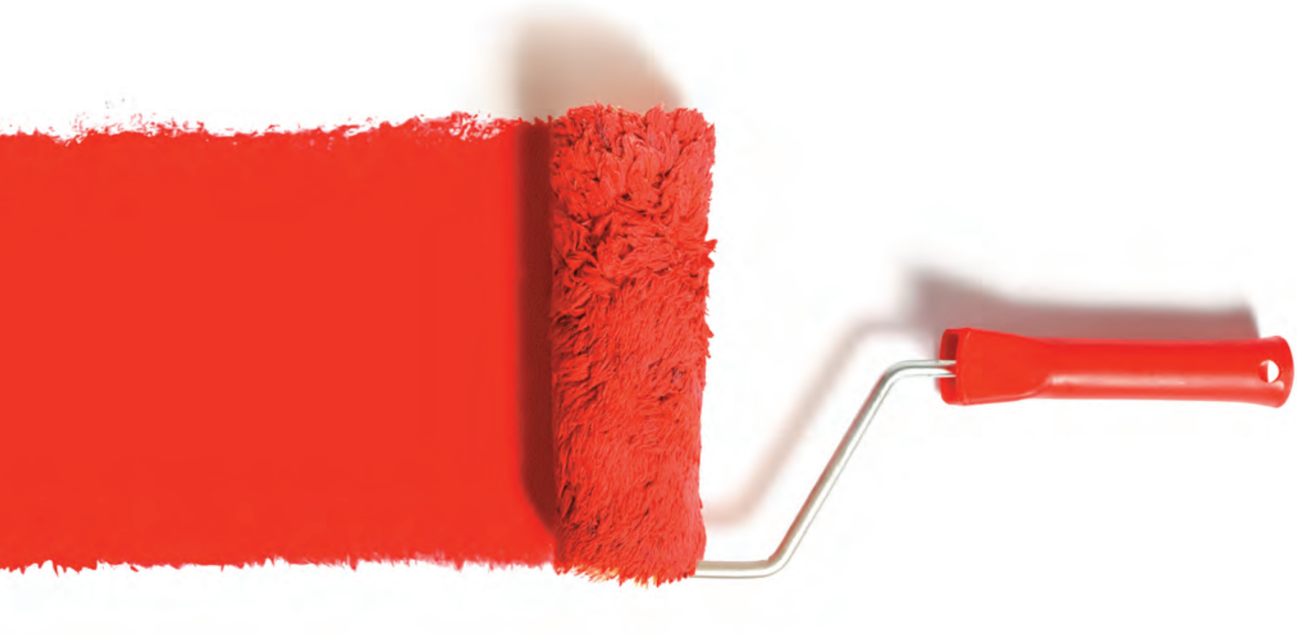
facts

Xanthan Gum in paints



Introduction

As in other industries, green solutions and sustainability have been key initiatives in the paints and coatings industry. Coatings have many functions beyond aesthetics, one of which is increasing the lifespan of structures and equipment. In a way, the act of coating a substrate is itself inherently sustainable. That said, there is still a need for sustainable and bio-based raw materials that function just as well as their traditional counterparts in order to ensure coatings applications still achieve the same level of quality.

Jungbunzlauer is a world leader in sustainable, natural-based raw materials that make products safer and more effective. Jungbunzlauer's xanthan gum is one such material, as it has a broad range of benefits for water-based paint and coating formulations. In this brochure, we will discuss its function as a thickener in architectural coatings and introduce a new grade of it designed specifically for paints.

The function of rheology modifiers in paints

Specific regulations requiring low to zero volatile organic compounds (VOCs) have become increasingly widespread, especially in architectural coatings.[1] Subsequently, the market for waterborne coatings has continued to expand.[2] Due to water's chemical nature as a solvent, water-based paints often require specialised additives to perform similarly to solvent-based formulations. One important class of compounds utilised in waterborne paints are rheological modifiers or thickeners. Their importance stems from their influence over the paint's rheology, i.e. the science of flow and deformation. Flow properties are especially important, as they govern many facets of paint's performance. This includes everything from controlling the settling of pigments during storage to the amount of paint taken up by the brush or applicator and the flow properties of the film once it has been applied to a surface. In terms of flow properties, a thickener's effect on the sag and levelling needs to be considered, since a balance exists between the two. The quality and gloss of the paint must also be taken into account when making decisions about which thickeners to use.

Xanthan gum is a high-molecular weight polysaccharide that forms very thick solutions with low concentrations, which remain uniquely stable over a wide pH and temperature range. Even more interesting is its pseudoplastic behaviour, which allows thickened xanthan gum solutions to be easily pumped, poured or sprayed. These properties have made xanthan gum a top choice in the food industry for thickening applications such as dressings or sauces. This aspect also makes xanthan gum an attractive thickener for paint applications, where its high viscosity in the low-shear range can produce excellent results in the stabilisation of formulations and sag resistance.

From traditional thickeners to innovations

Cellulosics, especially hydroxyethyl cellulose (HEC), have historically been the primary class of thickeners used in waterborne paints. They show effective resistance to sag and settling, and generally have good compatibility with other additives and pigments. However, high sag resistance has led to issues with levelling because the paints thicken too quickly. In addition, paints thickened with HEC have a tendency to cause spattering when applied via roller. The use of a lower-molecular weight (MW) HEC addresses these problems. However, such an HEC produces excessively shear-thinning solutions, which can cause difficulty when applying the paint.[3]

Associative thickeners are a class of rheological modifiers that minimise some of the issues with cellulosics. A broad range of associative thickeners exists: alkali swellable emulsions (ASEs), hydrophobically modified ASEs (HASEs) and hydrophobically modified ethoxylated urethane (HEUR) are some of the most common types. Paints formulated with associative thickeners tend to be less shear thinning than those thickened with cellulosics. As a result, a thicker wet film is applied, which alleviates issues with levelling. However, the mechanism behind the thickening behaviour is complicated and small changes to formulas, particularly with pigments, can cause undesired outcomes.[3]

Many modern latex paint formulas, especially high-gloss formulations, will use combinations of rheological modifiers. Typically, these are associative thickeners in combination with HEC. This ensures a good balance between the low-shear and high-shear viscosity ranges, and improved compatibility with pigments.

Previous work with xanthan gum in paint formulations suggested benefits over cellulosics. Higher viscosity in the low-shear range suggests improved stabilisation and xanthan gum may be inherently less prone to spattering. Given that it is common practice to use a combination of thickeners, we compared the performance of xanthan gum to HEC in combination with a commercially available associative thickener (HEUR). Through our research, we also identified a new grade of xanthan gum that is especially well-suited for paint applications.

Xanthan Gum – made naturally by fermentation

HEC and other cellulose thickeners are produced by chemically treating cellulose. Although cellulose is a very common biopolymer, it can have disadvantages if used as thickener. The cellulose extracted from natural sources does not demonstrate the desired thickening properties. Therefore, it has to be dissolved or chemically activated to make the polymer chain accessible to chemical modifications. The strong hydrogen bonding between the chains requires special solvent systems. The latter often include the addition of salts, strong acids and bases or organic solvents that have a negative impact on the environment. The activation of the cellulose is done under high pH conditions, which leads to a derivate called alkaline cellulose.[4]

Once the cellulose polymer has been activated, chemical groups can be introduced. In the case of HEC, alkaline cellulose is treated with ethylene oxide. For other cellulose thickeners, chloromethane, propylene oxide, chloroacetic acid or combination thereof are used. After the so-called hydrophilisation (etherification reaction), the cellulose derivatives are then purified.[5]

While cellulose is naturally derived, it requires chemical treatment to obtain the properties desired. This can have a negative impact on the application or the customer's expectations if the latter is looking for a more natural paint formulation.

Xanthan gum is obtained by the fermentation of glucose from, e.g. corn starch. During this process, bacteria produce the thickener directly in its final form. The xanthan gum is separated from the fermentation brew by precipitation using an alcohol, which can be recovered after the solids are dried. Xanthan gum is obtained as free-flowing powder. When dissolved in an aqueous phase, it can be immediately used as a thickener without any further chemical treatment. Due to the nature of fermentation, xanthan gum is not at risk of being contaminated by hazardous chemicals, which reduces the environmental impact.

Usually technical grades, readily dispersible grades or grades with reduced pseudoplasticity can be used for water-borne paint formulations. The different grades are obtained by variations in the manufacturing process. There are also grades available that show improved salt tolerance or fast hydration in aqueous media. Table 1 shows the xanthan gum grades from Jungbunzlauer, which were used in this study.

Table 1: Used xanthan gum grades

Xanthan Gum grade	Description
XG 1	Technical grade with reduced pseudoplasticity
XG 2	Standard technical grade
XG 3	Technical readily dispersible grade

Xanthan Gum for brush/roller applications

Background

Initial tests proved promising for xanthan gum as a replacement for cellulosics in a standard architectural semi-gloss paint formulation. Through this testing, we identified one xanthan gum grade (XG 1) that had rheological characteristics very similar to a standard, high-MW HEC. However, this grade of xanthan gum offered a better balance between sag and levelling, which warranted further investigation. Specifically, we evaluated in-can stability and spattering characteristics.

Paint preparation process and formulation recipe

A standard, flat architectural coating acted as the basis for the test formulation. A detailed description of the formulation can be found below in table 1. Since the associative thickener (Acrysol RM™ 825) was used in previous tests, it was included in this formulation as well. Preparation was broken up into three distinct steps. As a first step, the hydrocolloid thickeners (xanthan gum or HEC) were added and allowed to hydrate prior to the pigment grind stage. This second step was complete once the appropriate grind rating was achieved. The third step comprised the letdown or thindown phase. Here, the grind is diluted with the less viscous remaining formulation components. The letdown components were thus sequentially added by stirring them into a vessel containing the grind mix. The concentrations of the main thickener and the associative thickener (HEUR) were kept constant at either 0.25% or 0.15% throughout this study, while the main thickener type was varied. As noted previously, we chose to evaluate Jungbunzlauer's xanthan gum grade XG 1 in comparison to HEC (that included both a high- and a low- MW HEC). Jungbunzlauer's xanthan gum grade XG 3 was also chosen for the same purpose. This grade is treated with glyoxal for enhanced dispersibility.

Table 2: Formulation used for roller-coating evaluation

Component	Supplier	Function	Parts by weight/g
1st step: Mixing – low shear 700 rpm			
Water (DI)		Solvent	81.5
Xanthan Gum or others	Jungbunzlauer	Rheology modifier	0.8
Sodium hydroxide, 10%	VWR	pH adjustment	0.6
Dispex® CX 4248	BASF	Dispersing agent	4.2
KathonTM LXE	DOW	Preservative	0.6
FoamStar® ED 2523	BASF	Defoamer	0.6
2nd step: Grind stage – pigment preparation – high shear 2000 rpm			
Tioxide® R-TC90	Venator	TiO_2, white pigment	24.0
Omyacarb® 2GU	OMYA	$CaCO_3$ filler	75.8
Omyacarb® 5GU	OMYA	$CaCO_3$ filler	66.7
3rd step: Let down – low shear 700 rpm			
FoamStar® ED 2523	BASF	Defoamer	0.6
Loxanol®CA 5308	BASF	Coalescing agent	3.0
Acronal® S790	BASF	Binder	39.9
AcrysolTM RM-825	DOW	Rheology modifier (HEUR)	0.5
Water (DI)		Solvent	1.2
			300

Test methods

Viscosity profile

We used a rheometer with cone-plate geometry (C 35/2TiC; Haake™ RheoStress™ 1, Thermo Fisher Scientific) to measure the viscosity of the paints. The shear rate varied between 0.1 s^{-1} to 1000 s^{-1}. The low-shear rate covered the storage stability, and levelling and sagging behaviour of the paint. The high-shear rate represented the application of the paint on the wall, e.g. via spraying. During the measurement, the temperature of the sample was kept at 25°C.

Stability measurements

For the storage stability tests, approximately 30 ml of the paint formulation was filled into screw-cap bottles and stored at 40°C. Over a period of two months, the stability was checked and the status was documented with a picture on a weekly basis.

Spatter tests

Here we investigated paint's tendency to spatter. First, the paint was applied onto a black plastic panel (Leneta Scrub Test Panels; 20 cm x 15 cm) with an applicator frame to achieve a wet film thickness of 125 µm. This black plastic panel was vertically attached onto a wall 2.5 cm above the test table. A second black plastic panel (20 cm x 15 cm) was placed on the table. With a clean, dry roller (roller width: 6 cm), the paint was rolled out up and down with similar force and speed ten times. A metronome set at 80 bpm was used to ensure consistency with the speed. The quantity and size of the spatters on the second black plastic panel were evaluated and categorised afterwards. The examples of the ASTM D4707-09 were used for the evaluation.

Results

Viscosity profile of pure thickener solutions

Prior to the formulation work, we evaluated and compared the rheology of the pure thickeners: several xanthan gum grades, and one low-MW and one high-MW HEC. Figure 1 displays the different rheological profiles of the thickeners in a 0.4% by weight solution. Each grade of xanthan gum exhibits its typical shear-thinning behaviour. The viscosity of the HEC grades is heavily dependent on the MW. The biggest difference exists in the low-shear range. Xanthan gum exhibits a much higher viscosity in this range. Overall, this evaluation allowed for a better understanding of the rheology of the different thickeners across a broad shear range and gave some insights into why xanthan gum offers better control of pigment settling.

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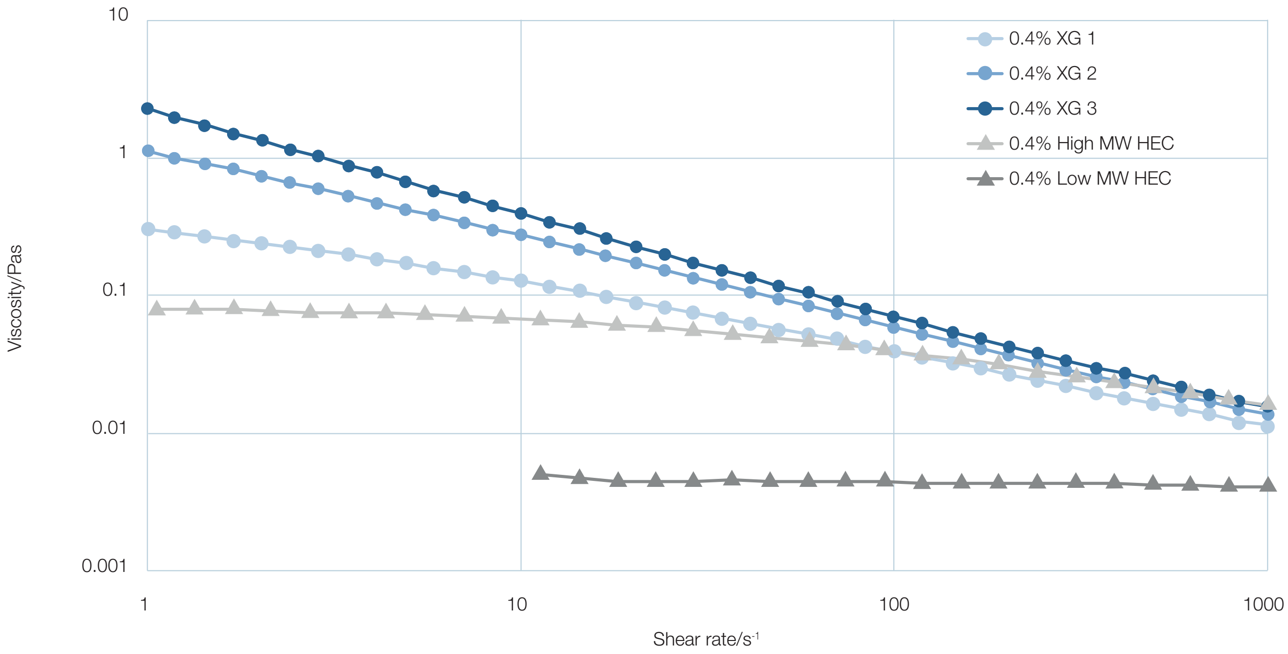
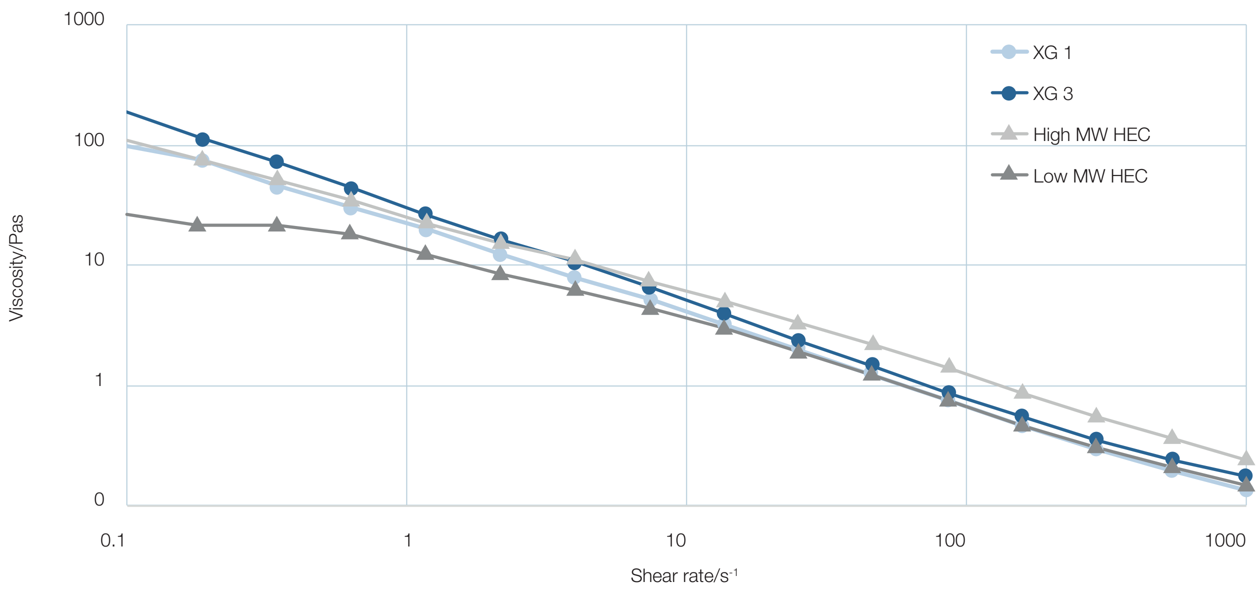
Figure 1: Steady-state viscosity as a function of the shear rate for aqueous solutions (0.4% by weight) prepared with the thickeners



Viscosity profile of formulations with different thickener

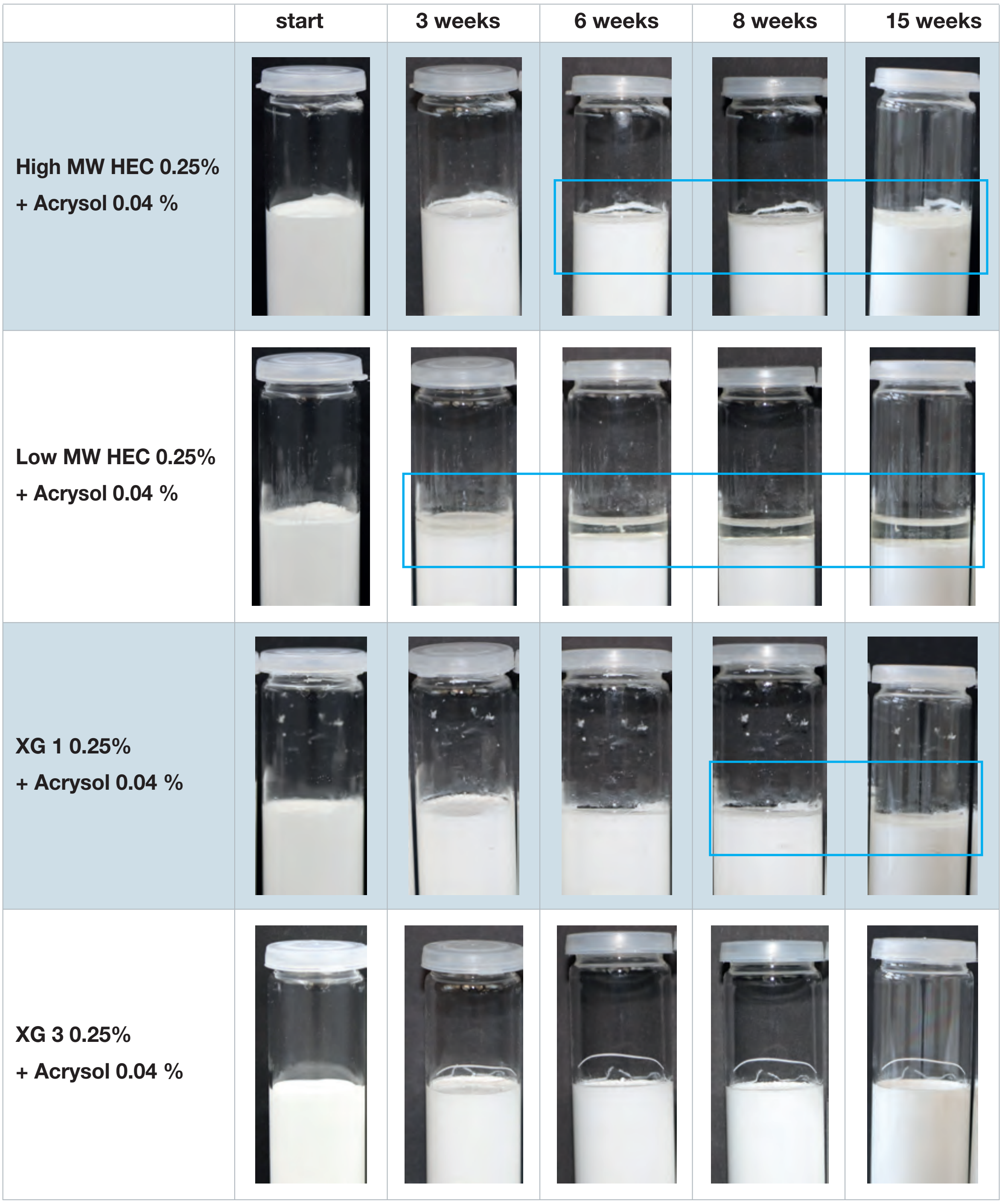
The steady-state viscosity profiles of the paint formulations are shown in Figure 2. The lower-MW HEC formulations have the lowest low-shear viscosity while the XG 3 has the highest low-shear viscosity. The XG 1 formulation and the high MW HEC formulation show very similar low-shear viscosities in the formulation. However, as previous studies have shown, we see slight differences in sag performance and pigment stabilisation.

Figure 2: Steady-state viscosity as a function of the shear rate for the different paint formulations



Stability measurements
The results for the stabilisation study can be found in figure 3. The shelf stability study shows that the lower-MW HEC begins phase separation the quickest, at only three weeks. High-MW HEC begins to show very slight syneresis at the six-week mark despite similar low-shear viscosity. Only at the eight-week mark is slight syneresis observed with the XG 1. The XG 3 displayed superior syneresis control throughout the entire study. Overall, xanthan gum displays a tendency to stabilise systems much better than HEC.

Figure 3: Stabilisation results; the light blue bar represents the time frame when syneresis was observed



Spatter tests
Table 3 summarises the results of the spatter study. One large differentiating factor between xanthan gum and HEC was xanthan gum's ability to resist spatter, particularly the XG 1 formulation. Aside from the overall viscosity of the formulation, the elasticity of the aqueous phase influences the spattering, which is related to the extensional viscosity. The long polymer chains of HEC give solutions high extensional viscosity.[6] The structure of xanthan gum in solution is hypothesised to impart a lower extensional viscosity. Contrary to other research, the low-MW HEC shows a lower spatter resistance. Because the thickener concentration was kept constant in this study, the low-MW HEC gives the formulation a lower viscosity profile than the high-MW HEC (see figure 3). The lower viscosity profile seems to outweigh the effect of the reduced extensional viscosity resulting in an increased spattering compared to the high-MW HEC.

Table 3: Spatter test results

Formula	Observation
XG 1	Low spattering
XG 3	Some spattering
High-MW HEC	Some spattering
Low-MW HEC	High spattering

Xanthan Gum for spray applications

Introduction to spray applications
A variety of application methods can be utilised to apply paints and coatings to a surface. One of the most common techniques for industrial coatings is spraying. Here, paints are homogeneously applied via many different techniques ranging from conventional air spraying to high volume low pressure (HVLP) and airless, airmix, electrostatic (ESTA) techniques. Since the nature and rheology of paints differ, various parameters of the spray gun need to be optimised. Nozzle size, operating pressure and operating speed can be adjusted with respect to the desired application.

Spray applications provide a fast and economical way to apply high-quality coatings. One essential advantage of spray application versus conventional brush or roller application is the speed, especially if larger areas need to be painted. By drastically reducing the time of the painting job, it leads to a significant cost reduction. With optimised parameters, spraying allows for a better cost-in-use and generally produces a smoother paint surface and better finish compared to the other techniques as it avoids brush strokes and roller imprints.

Another benefit of the spray application is the easy accessibility of more complex substrates (i.e. 3D or uneven surfaces). Roller coaters, by contrast, cannot be used at all on such surfaces, and even with brushes of different shapes and sizes, a homogeneous surface coverage with paint is not easy to do.

In this article, we focus on the spray application of an architectural paint formulation.

Formulation
The architectural paint formulation we used is shown in table 4. The preparation process consisted of three main steps. In the first step, the thickener was dissolved in water, and afterwards the dispersing aid, the preservative and the defoamer were added under low shear. In the second step, the pigments and fillers were added and subsequently ground under high shear at 2000 rpm for 20 minutes. In the last step, the binder, coalescing agent, additional water and defoamer were added under low shear. While the thickener concentration was kept constant at 0.4% throughout this study, the thickener type varied. Different xanthan gum grades (XG 1, XG 2, XG 3) were tested and the properties were compared to a cellulose-based thickener like hydroxyethyl cellulose (HEC).

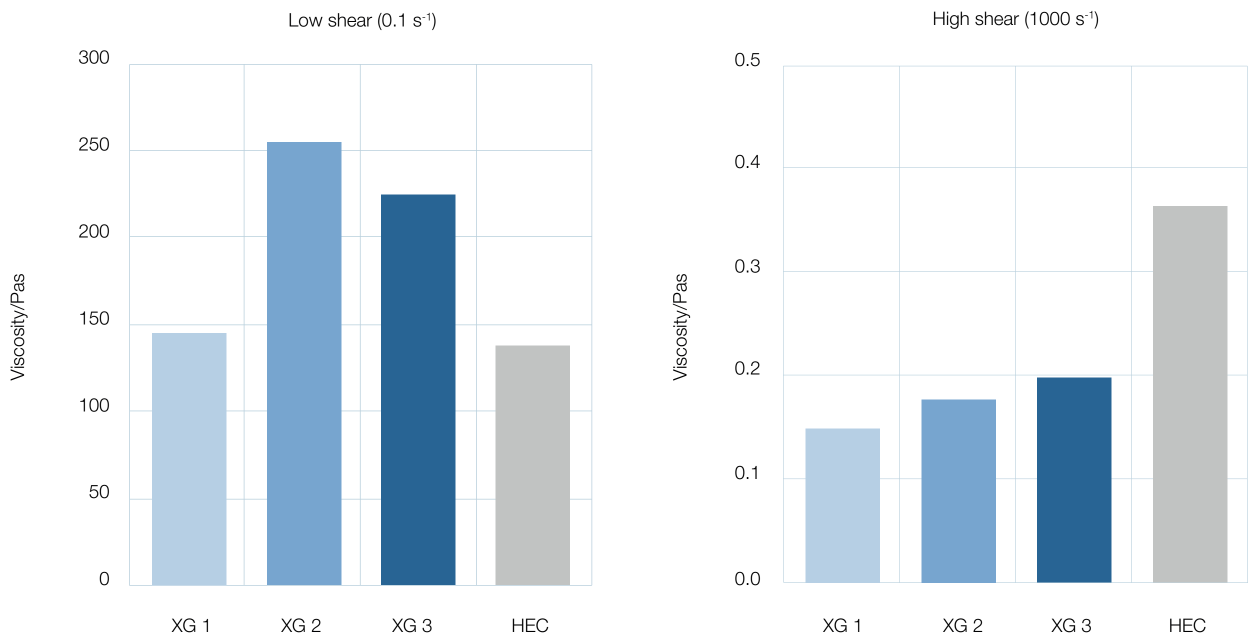
Table 4: **Formulation recipe for a conventional flat interior paint**

Component	**Supplier**	**Function**	**Parts by weight/g**
1st step: Mixing – low shear 700 rpm			
Water (DI)		Solvent	81.0
Xanthan Gum or others	Jungbunzlauer	Rheology modifier	1.2
Sodium hydroxide, 10%	VWR	pH adjustment	0.6
Dispex® CX 4248	BASF	Dispersing agent	4.2
KathonTM LXE	DOW	Preservative	0.6
FoamStar® ED 2523	BASF	Defoamer	0.6
2nd step: Grind stage – pigment preparation – high shear 2000 rpm			
Tioxide® R-TC90	Venator	TiO_2, white pigment	24.0
Omyacarb® 2GU	OMYA	$CaCO_3$ filler	75.8
Omyacarb® 5GU	OMYA	$CaCO_3$ filler	66.7
3rd step: Let down – low shear 700 rpm			
FoamStar® ED 2523	BASF	Defoamer	0.6
Loxanol®CA 5308	BASF	Coalescing agent	3.0
Acronal® S790	BASF	Binder	39.9
Water (DI)		Solvent	1.8
			300

Rheology

The effect and performance of a thickener can be analysed in the rheological behaviour of the paint formulation. Hence, viscosity measurements were conducted at a broad range of shear rates. In Figure 4, the viscosities determined at low shear ($0.1\ s^{-1}$) and at high shear ($1000\ s^{-1}$) are shown. All xanthan gum grades yielded a higher low-shear viscosity than the HEC reference, which indicates a better stabilisation effect. In the case of the high-shear range, a lower viscosity was obtained. Lower viscosity can be an advantage for the spraying process since the application is easier and faster. Additionally, a low high-shear viscosity results in a spraying system that necessitates lower air pressure.

Figure 4: **Viscosities of the paint formulations containing the different thickener types: three XG grades and one HEC thickener**



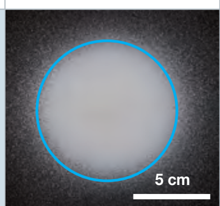
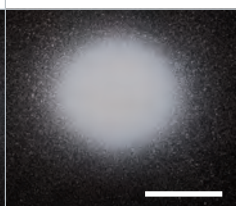
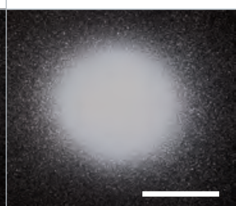
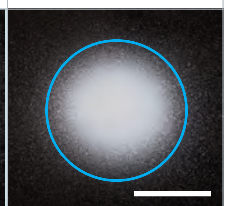
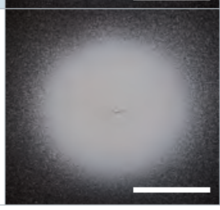
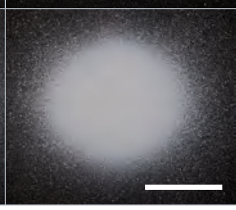
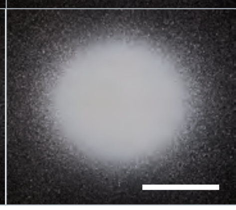
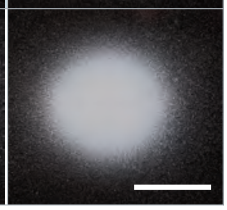
Spray applications – test setup
For the spray applications, a conventional air spray gun from SATA (SATAjet 1000 B RP) was used. This device is shown in figure 5. The spray gun utilises compressed air to atomise (break up) the paint and apply it to the surface. Paint and air are fed into the gun through separate channels and are mixed using an air cap. Under the proper conditions, the air-paint mixture forms a controlled pattern, known as a 'fan'. Figure 5 shows the difference between a poorly and a well-defined fan. For all tests, a constant pressure of 2 bar was applied. The distance of the gun to the sheet was kept constant as well. Each paint formulation was applied to the substrates in a well-defined spray time. After drying at room temperature, the spray pattern was visually evaluated.

Based on the respective spray pattern, different gun parameters like nozzle size, and spray time were optimised.

Figure 5: Spray gun (left) as well as a poorly (middle) and a well-defined (right) spray 'fan'

Results – spray tests with different xanthan gum grades and comparison to the cellulose-based thickener HEC
The results of the spraying experiments are shown in figure 6. The two blue circles in figure 6 have the same diameter and are placed over the photo to highlight the different sizes in the spray pattern. For the spraying tests, a nozzle size of 1 mm was chosen and the spraying time varied between 3 and 5 seconds. Based on the rheological profile, all xanthan gum grades showed a larger covered area as compared to the HEC-based formulation. This is due to the higher shear-thinning behaviour of the xanthan gum grades, which results in a more homogenous and broader spay pattern. Among the xanthan gum-based formulations, XG 1 exhibits the finest spray mist. XG 2 and XG 3 yielded a spray mist comparable to that of HEC. In addition, the high low-shear viscosity of the xanthan gum grades was beneficial in the spraying experiments as it prevented paint dripping after the spraying was done.

Figure 6: Spray patterns of the different paint formulations prepared with three different XG grades and one HEC-based thickener under different spraying conditions, as described on left

	XG 1	XG 2	XG 3	HEC
Nozzle: 1.0 mm, 3s				
Nozzle: 1.0 mm, 5s				

The three xanthan gum grades were also compared with two other cellulose-based thickeners: methylhydroxyethyl cellulose (HEMC) and carboxymethyl cellulose (CMC). This additional study revealed similar results as with HEC and can be shown upon request.

Summary

Xanthan gum has shown excellent rheological properties in architectural paint formulations and demonstrated high stabilisation of pigment particles. Good compatibility with other thickeners and ingredients allow for use in a variety of formulas, from flat paints to semi-gloss, depending on the requirements of the application. Xanthan gum is not only suitable for roller and brush application but also for spray applications. Its shear-thinning property enables an easy application, e.g. by a homogenous spray mist formation and a defined spray pattern, without drawbacks in sag resistance.

Using the xanthan gum grade XG 1 provides further benefits for paint formulators, delivering a similar rheology to classical water-soluble polymers like HEC with less spatter and enhanced stabilisation of pigment particles. For increased in-can stability, xanthan gum grades with high low-shear viscosity can reduce the occurrence of syneresis.

References

[1] www.coatingsworld.com/issues/2016-01-01/view_features/additives-industry-update-517038.

[2] www.european-coatings.com/Markets-companies/Five-facts-on-the-water-borne-coatings-market/.

[3] Jones, F.N.; Nichols, M.E.; Pappas, S.P.: Organic coatings: Science and Technology (4th ed.).

[4] Klemm, D.; Philipp, B.; Heinze, T.; Heinze, U., Wagenknecht, W. : Comprehensive Cellulose Chemistry (1st ed.), Wiley-VCH, Weinheim, 1998, vols. 1 and 2.

[5] Balser, K.; Hoppe, L.; Eichler, T.; Wandel, M.; Astheimer, H-J. in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 1986, vol. A5. 419–459.

[6] Tracton, A.A.: Coatings Technology Handbook (3rd ed.), CRC Press, Boca Raton, 2006.

About Jungbunzlauer

Jungbunzlauer is one of the world's leading producers of biodegradable ingredients of natural origin. We enable our customers to manufacture healthier, safer, tastier and more sustainable products. Due to continuous investments, state-of-the-art manufacturing processes and comprehensive quality management, we are able to assure outstanding product quality.

Our mission "From nature to ingredients®" commits us to the protection of people and their environment.

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