Artur Palasz, Ph.D., Spektrochem, reports on case studies comparing the effects of standard HEC with hydrophobically-modified HEC in latex paints

Hydrophobically-modified hydroxyethyl cellulose (hmHEC) – effective low-shear viscosity builder for latex paints

INTRODUCTION

Cellulose thickeners are the basic group of rheological modifiers ensuring the viscosity of dispersion paints in the low-shear (Brookfield) and mid-shear forces (Stormer) area. They provide resting viscosity and allow the paint structure to be rebuilt after application to the substrate at higher shear rates (e.g. roller), preventing sagging. Standard grades of hydroxyethyl cellulose as paint thickeners are common and used in both high and low PVC (pigment volume concentration) latex paint formulations. In low-cost contractor's dispersion paints with very high PVC (e.g. ceiling paints), HEC also acts as a binder supporting the binding of pigments and fillers. Unfortunately, typical HEC thickeners do not allow for non-spattering properties when painting with a roller, and such a feature is extremely desirable for the paint market, especially where interior painting is performed by non-professional painters. The solution to this problem comes with hydrophobically-modified HEC thickeners, the effectiveness of which will be discussed in this article.

FROM CELLULOSE TO CELLULOSE DERIVATIVE THICKENERS

Cellulose thickeners are cellulose ethers derived from pure cellulose, which are subjected to alkalisation and then substitution of the obtained alkaline cellulose with e.g. ethylene oxide to obtain hydroxyethyl cellulose (HEC), sodium monochloroacetate to obtain carboxymethyl cellulose (CMC) or with methylene chloride to obtain methyl cellulose (MC) (**Figure 1**).

Further reactions and processing are carried out in order to obtain complex substitutions, such as e.g. hydroxypropylmethylcellulose (HPMC) or methylhydroxyethylcellulose (MHEC) (**Figure 2**).

The cellulose ethers obtained in this way are characterised by the degree of substitution defined as the average number of hydroxyl groups substituted for the anhydro glucose unit, and the molar degree of substitution defined as the average number of moles substituent for the anhydro glucose unit. Cellulose ethers are thickeners that create a structure by associating particles with a dispersion binder and also forming a swollen gel in an aqueous medium.

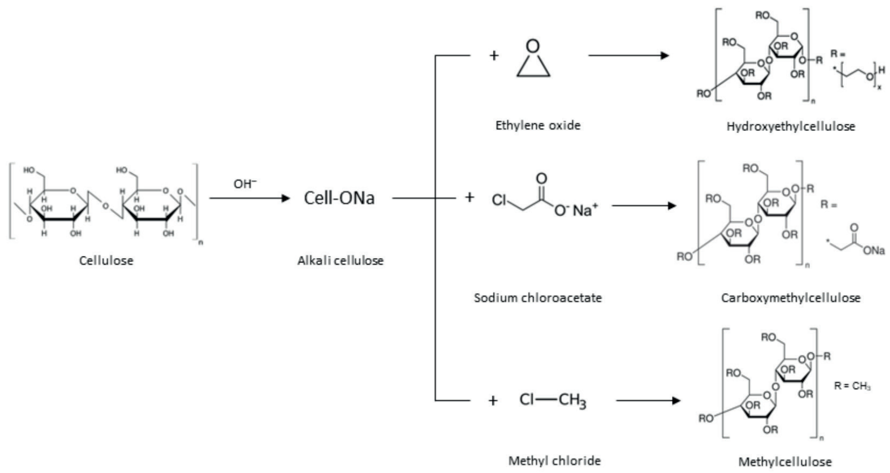

Figure 1. Examples of reaction mechanisms for the formation of cellulose derivatives as thickeners

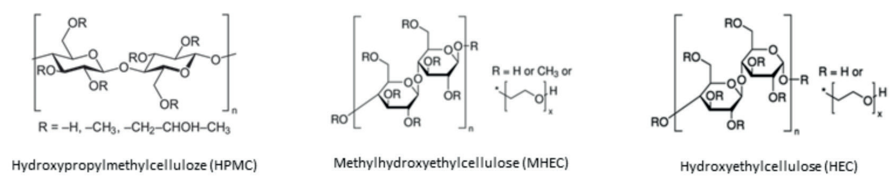

Figure 2. Examples of cellulose ether substitutions

Cellulose thickeners owe their efficiency of rheology to dispersion paints to the associative effect, building network and a swollen gel in an aqueous medium through association with particles of polymer dispersion, but also parts with pigments, fillers and surfactants. Water solubility is favoured by the hydrophilic nature of the cellulose ether chain, and the rate of dissolution in water is caused by modification with substances responsible for delaying dissolution in water, e.g. glyoxal. The hydrophilic nature of cellulose ethers, e.g., hydroxyethyl cellulose, gives them good solubility in water, but the associative effect is not very strong. Its increase is usually controlled by increasing the proportion of HEC in the formulation and using higher viscosity ethers. Such HEC thickeners, however, tend to spatter in latex paints during roller coating due to a too weak associative effect. In paints with HEC cellulose ether as the sole or major rheology modifier, there is a problem with spattering during roller coating.

The solution to this problem is the hydrophobic modification of the HEC chain with e.g. polyoxyethylene cetyl ether or 2-[2-[2-[2-[2-[2-[2-[2-[4-(2,4,4-trimethylpentan-2-yl)phenoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethanol via HEC reaction in water (with IPA mixture) in the presence of NaOH for several hours at 80°C, followed by filtration and drying. As a result of such modification, a hydrophobically modified HEC (hmHEC) (**Figure 3**) is formed, which due to the presence of a hydrophobic chain is able to cause a stronger associative effect with the dispersion binder particles and is responsible for reducing spattering during painting with a roller.

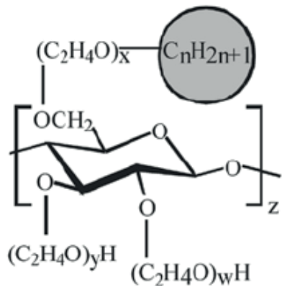

Figure 3. Structure of hydrophobically-modified HEC

The stronger associative effect is also conducive to increasing the viscosity in the area of low and medium shear rates, improving the elimination of syneresis (squeezing water onto the surface of the paint in the package), better tint viscosity stability, i.e. viscosity retention when tinting with pigment concentrates, eliminating sagging and improving viscosity stability over time.

EXPERIMENTAL

In order to present the effects of hydrophobically-modified HEC in dispersion paints, a comparison of the standard HEC and hmHEC varieties was carried out in the formulation of PVC 72% paint based on Revacryl UltraGreen 3710 styrene-acrylic copolymer dispersion by Synthomer. A very simple formulation was intentionally prepared (see **Table 1**) to better illustrate the associative effect undisturbed by any other additives.

Two paints of 0.8% by weight in the HEC and hmHEC formulations were prepared for the tests. HEC with a viscosity of ca. 6.000mPa · s (2% in water) and hmHEC with a viscosity of max. 500mPa · s (1% in water). The names of the cellulose ethers used were not given due to the coverage of the non-disclosure agreement (NDA).

Formulation characteristics:

- PVC: 72%
- CPVC: 63.7%
- Q (PVC/CPVC): 1.13
- Solid content: weight: 54%, volume: 33% (calculated)
- Paint density: 1.45g/cm^3, weight per gallon: 12.13lbs/gal

A set of laboratory tests was carried out on the prepared paints in accordance with the specified procedures, standardised with the use of equipment ensuring the appropriate precision of measurements:

Table 1. Formulation used in case studies of HEC/hmHEC thickeners

Raw materials	Kilograms	Litres	Pounds	Gallons	Function	Supplier
Mill base (cowles dissolver)						
Demineralised water	39.86	57.99	87.8	58.19	Carrier	
Calgon N	0.12	0.14	0.26	0.14	Wetting agent	ICL Group
Darvan 7N	0.12	0.15	0.26	0.15	Dispersant	Vanderbilt
Acticide MBS	0.20	0.27	0.44	0.27	In-can biocide	Thor
Byk 014	040	0.60	0.88	0.61	Defoamer	Byk Chemie
Tytanpol R-001	10.0	3.93	22.2	3.91	TiO_2 pigment	Azoty Police
Omyacarb 5VA	37.0	19.92	81.5	19.98	GCC filler	Omya
HEC / hmHEC	**0.8**	**0.65**	**1.76**	**0.65**	**Thickener**	**confidential**
High speed disperse for 15 minutes *Let-down (anchor stirrer)*						
Revacryl UltraGreen 3710	11.50	16.07	25.3	16.11	S/A binder	Synthomer
Mix at low speed for 10 minutes						
Total:	100	100	100	100		

- Brookfield apparent viscosity (low-shear viscosity), ASTM D2196 method A, samples prepared before measurement according to ASTM D2196 section 7, temperature: 23-24°C
- KU viscosity (mid-shear viscosity), ASTM D562 method B (by BYK byko-visc DS Stormer viscometer), measurement at 23°C
- Anti-Sag Index, ASTM D4400, test with Leneta ASM-4 multinotch applicator. This is not the wet film thickness but the gap where the Anti-Sag Index is determined with the calculation according to the standard ASTM D4400.
- Spatter resistance, ASTM D4707, test with spool notch roller (0 – poor, 10 – no spatter)
- Storage stability (1 month at 52°C), ASTM D1849 with evaluation of syneresis (internal lab procedure with rating of syneresis: 0 – significant, 2 – considerable, 4 – moderate, 6 – slight, 8 – very slight, 10 – no syneresis).

TEST RESULTS AND DISCUSSION

Below are the results of tests carried out within the scope of the project.

Viscosity

Figure 4 shows a comparison of low-shear viscosity (Brookfield apparent viscosity) which shows a significant difference between the tested standard variant of HEC and hmHEC. Brookfield viscosity at 5rpm is 184% higher for the hmHEC-based paint compared to the viscosity at 5rpm for standard-grade HEC. At 10rpm, this difference drops to 142% in favour of hmHEC showing very high associative efficiency of hydrophobically modified HEC, especially in low shear regions.

In **Figure 5**, the results of the measurements of the viscosity of paints using a Stormer light speedometer also show a significant associative efficiency of the hmHEC grade, the mid-shear viscosity of which is 14 KU higher than the standard HEC thickener.

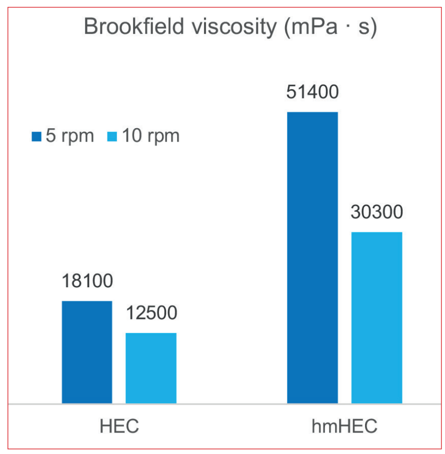

Figure 4. Brookfield viscosity test results

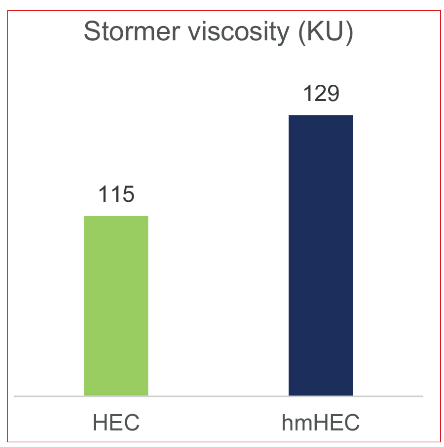

Figure 5. KU viscosity test results

Sagging

The sagging test shown in **Figure 6** illustrates how the associative effect obtained by HEC hydrophobisation helps to keep thickness when flowing down from vertical surfaces, also when adding a POS-tinting pigment concentrate. Viscosity retention and sagging inhibition is perfect with hmHEC while the standard HEC variation does not fully allow for thick wet-application of paints, especially after tinting.

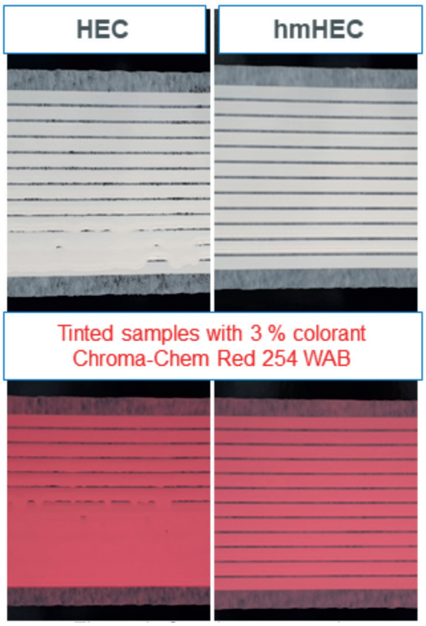

Figure 6. Sagging test results

Table 2. Test results of Anti-Sag Index

Paint sample	HEC	hmHEC
White base	(440µm) 17.6mils	(600µm) 24mils
Tinted by 3wt% colourant PR254	(290µm) 11.6mils	(600µm) 24mils

Table 2 presents the results of the Anti-Sag Index defining the height of the gap of the multinotch applicator, which allows one to obtain stripes of wet paint that do not run off.

Spattering

The spattering test, which simulates the application of paint on the wall with a roller, allows the reproducible assessment of how the paint splashes regardless of the type of roller and its pile length. **Figure 7** shows the photos of the test results and the grades obtained. The assumptions of enhancing the associative effect and minimising the spattering effect during roller painting turned out to be correct. The paint with hmHEC has a rating of 9, while the paint on the standard HEC variety has a rating of 6. The pictures show how significant difference in spattering reduction was achieved by replacing standard HEC thickener by hydrophobically modified HEC.

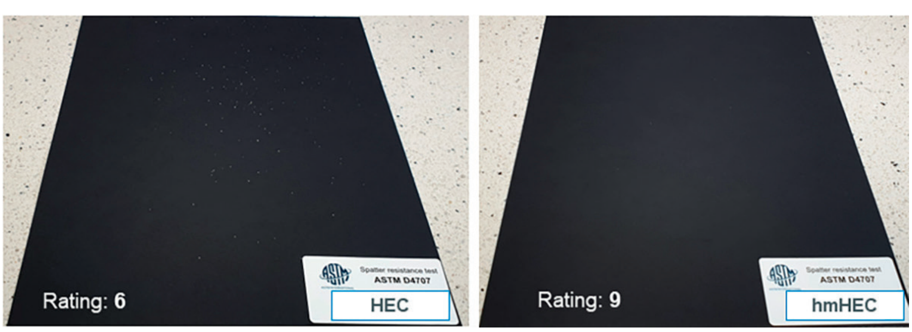

Figure 7. Spattering test result in the form of collected paint drops on a black cardboard

Figure 8. Syneresis evaluation result after storage stability test

Storage stability

An accelerated stability test conducted to assess syneresis and viscosity changes after storage allowed for further confirmation of the enhancement of associative thickening. The paint with HEC thickener shows moderate syneresis after 1 month at 50°C (rating: 4), while the paint with hmHEC does not show syneresis (rating: 10 no syneresis). The enhanced associative thickening mechanism allows for stability without squeezing water onto the paint surface and no unsightly water film is formed (**Figure 8**).

SUMMARY

The discussed results of the case studies and the comparison of the standard HEC variant to the hydrophobically modified HEC confirm the assumptions that the associative effect is much stronger due to the presence of hydrophobic substitution in the cellulose ether chain, which supports the connection with the particles of polymer dispersion, but also pigments, fillers and surfactants, which are also mostly hydrophobic. Strengthening the associative effect translates into an improvement of sagging (also after tinting), spattering, important from the point of view of application, as well as viscosity at low shear rates and elimination of syneresis, which in turn is very important when storing paints in packaging.

The use of hmHEC allows the formulator to obtain the desired viscosity values both in the low-shear (Brookfield) and mid-shear (KU viscosity) regions and to adjust the viscosity at the level of 90-110 KU. These benefits make hmHEC an interesting raw material and its performance furnishes the desired properties, so valuable on the worldwide market of dispersion architectural paints.

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Author: Artur Palasz, Ph.D.
SPEKTROCHEM - Technical Center of Raw Materials for Architectural Paints, Poland
Email: artur.palasz@spektrochem.pl