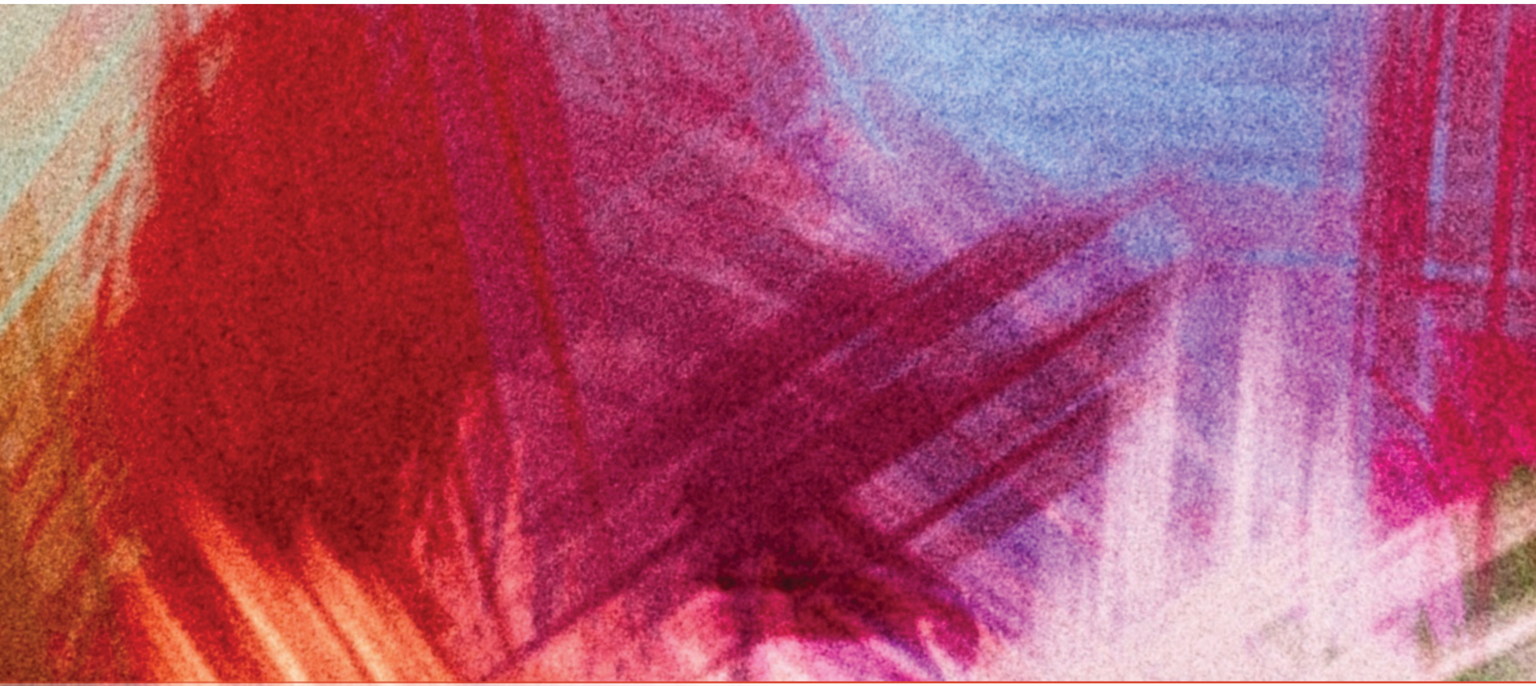
The Impact of **Microfibrillated Cellulose** on the Rheology of Water-based Acrylic Satin Paint upon Tinting

In this article, the authors will demonstrate how MFC can improve the resistance to viscosity loss upon tinting without sacrificing the flow/leveling properties of the coating.



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Associative thickeners are commonly used to thicken water-based coatings. Their mechanism of action is based on the hydrophobic interaction between the hydrophobic polymer groups as well as with the surface of the binder latex particles. It is commonly known that associative thickener-based formulations are prone to viscosity loss upon tinting due to the surfactants present in the tinting systems, leading to poorer sag resistance.

In this work, the effect of an insoluble microfibrillated cellulose (MFC) was studied on the prevention of viscosity loss on tinting with a deep tone base, formulated with two different hydrophobically modified polyurethane associative thickeners (HEURs), combined with a non-associative MFC thickener. The formulations were evaluated in terms of rheology, viscosity, sag resistance, flow/leveling, and gloss.

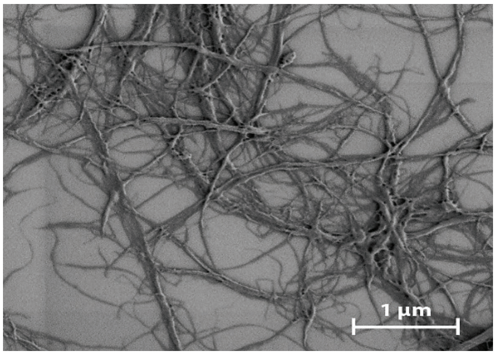
We will demonstrate how MFC can improve the resistance to viscosity loss upon tinting without sacrificing the flow/leveling properties of the coating.

Introduction

It is commonly known that waterborne formulations still suffer from several issues, and it is not always possible to obtain the same performance as with solventborne systems. One of the typical challenges with waterborne systems is related to the behavior of rheology modifiers in these complex systems. The common rheology modifiers can be divided roughly into two categories: associative, such as hydrophobically modified alkali soluble modifiers (HASE) and hydrophobically modified ethylene oxide modifiers (HEUR), and non-associative, such as hydroxyethyl celluloses (HEC) and methyl hydroxyethyl celluloses (MHEC). The former is typically sensitive to the presence of surfactants, and this is often seen after the tinting of the base paint. By comparison, the latter often causes issues with water sensitivity of the coating. In most cases, the viscosity of the paint reduces either as a consequence of the disturbance in the associative network due to the surfactants present in the tinting paste or due to microbiological contamination.

Microfibrillated cellulose (MFC), a biobased and multifunctional product made of cellulose, consisting of fibrils with lateral dimensions below micron size and lengths up to micron in scale.[1] An example of this fibril structure is shown in **Figure 1.** The thickening mechanism of MFC is based on the physical entanglement of nanosized fibrils and hydrogen

FIGURE 1
Scanning electron microscope image of MFC.



bonding, leading to a robust network. The high yield stress of MFC prevents sagging along with settling of heavy particles, whereas the strong shear thinning property of MFC allows the spraying of thick formulations. The exceptional thixotropic behavior leads to excellent sag resistance combined with good flow/leveling properties.[2]

The compatibility and rheological behavior of MFC has previously been studied in water based acrylic and epoxy systems.[3,4] The results from these studies showed that MFC dispersed very well into the resins and showed good compatibility. In addition, the viscosity and sag resistance increased with increasing concentration of MFC. Furthermore, the dispersions were heat stable in terms of sedimentation and retention of rheological properties. An example of the compatibility and stabilization effects of the fibrils is shown in **Figure 2.** The interaction of the OH-groups, via hydrogen bonding, on the surface of the entangled fibrils and the components (before shear) allows the increased stability of the formulation. Under shear forces (during shear) the disruption breaks the hydrogen bonding between the fibrils and OH-groups with the other components. Introduction of new components, such as the binder, interact with the open structure of the fibrillar network. Once shearing has stopped (after shear) the OH-groups and fibrils envelop the binder along with the original components, in-turn reforming the hydrogen bonding, allowing for increased stability of the formulation as well as increased compatibility.

Materials and Methods

Commercially available MFC was used in this study (manufactured by Borregaard AS) containing 10 wt % MFC in water. The following universal colorants were used for tinting: Lamp Black, Red Iron Oxide, and Phthalo Blue (8 oz/gal). Sag resistance was determined according to ASTM D4440 by using byko-chart 2852 and a LENETA Anti-Sag Meter "ASM-4 MEDIUM-RANGE" (4 mils (100 µm) – 24 mils (600 µm)); flow/leveling was determined according to ASTM D4062. The rheology was measured with an Anton Paar rheometer using a bob and cup measuring geometry.

FIGURE 2
Effect of shearing the microfibrillar network and the interaction with additional components (black dots) before, during and after shear.

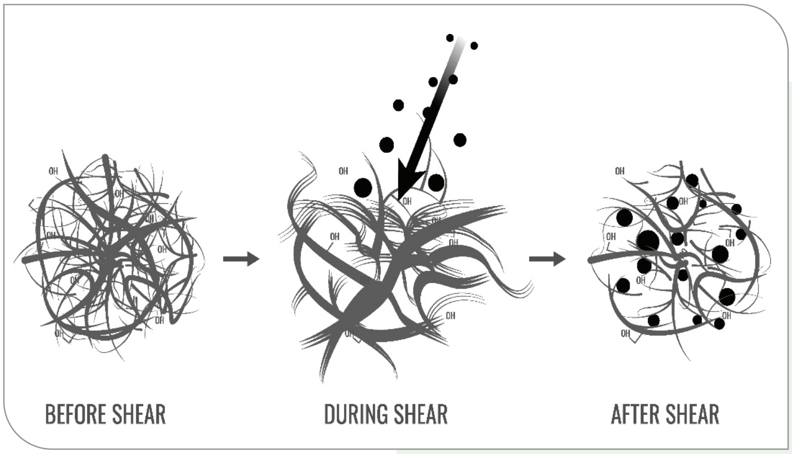


TABLE 1
Acrylic Binder Formulations

Components	HEUR A wt %	MFC B wt %	MFC C wt %
Binder *(Anionic Acrylic Co-Polymer Dispersion)*	59.6	59.6	59.6
Water	33.5	32.3	31.4
Defoamer	0.4	0.4	0.4
Rheology Modifier 1 *(Non-Ionic Low-Shear Thickening HEUR)*	2.2	–	–
Rheology Modifier 2 *(Non-Ionic High-Shear Thickening HEUR)*	3.2	3.2	3.2
Rheology Modifier 3 *(Non-Ionic Mid-Shear Thickening HEUR)*	1.1	2.2	1.9
MFC *(Biobased Rheology Modifier)*	–	2.3	3.5
Total (wt %)	**100.0**	**100.0**	**100.0**

Results and Discussion

Effect of MFC on the Rheology of an Acrylic Binder

A simplified binder formulation was first used for studying the impact of MFC on the viscosity after tinting of an acrylic waterborne system **(Table 1).** The formulation was based on an anionic dispersion of an acrylic copolymer containing Rheology Modifier 1, a HEUR for low-shear viscosity adjustment.

The strong impact of MFC to the low-shear viscosity of the formulations can be seen from **Figure 3.** Before tinting, the low-shear viscosity of the HEUR A formulation is 239 Pa.s, whereas the viscosity of the MFC B formulation is 964 Pa.s. After tinting, all low-shear viscosities of the HEUR-based systems decrease, most noticeably for the Lamp Black and Phthalo Blue formulations. In the case of both the MFC formulations (B and C), the low-shear viscosities increase dramatically when compared to the HEUR-based formulations both before and after tinting with all the tested universal colorants. Regarding the MFC C formulation, the low-shear viscosities actually have a large increase when a universal colorant is introduced, most notably with Phthalo Blue (2440 Pa.s. vs. 6340 Pa.s).

This noticeable increase in viscosity with MFC might be due to two reasons. Firstly, the physical entanglement of the nanosize fibrils and hydrogen bonding between the hydroxyl groups of MFC and hydrogen bonding compounds in the formulation are aiding the thickening effect. Secondly, the universal colorants typically contain glycol and glycol ethers, which are also known to strengthen the network of MFC. Based on these two reasons, the addition of MFC into the formulations positively impacts the low-shear viscosity on tinting, as seen especially with the MFC C formulations **(Figure 3).**

A three interval thixotropy test (3-ITT) was used to further understand the differences in the rheological behavior between the HEUR and the MFC after tinting the formulations, as shown in **Figures 4, 5, and 6.**

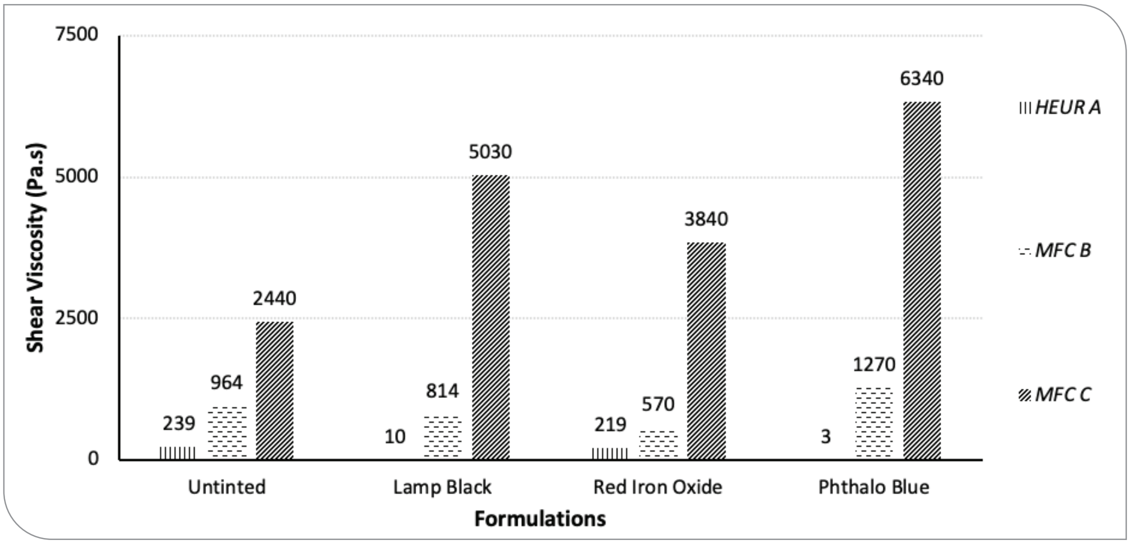


FIGURE 3 Low-shear viscosities for untinted and tinted (Lamp Black, Red Iron Oxide, and Phthalo Blue) formulations after 24 hours.

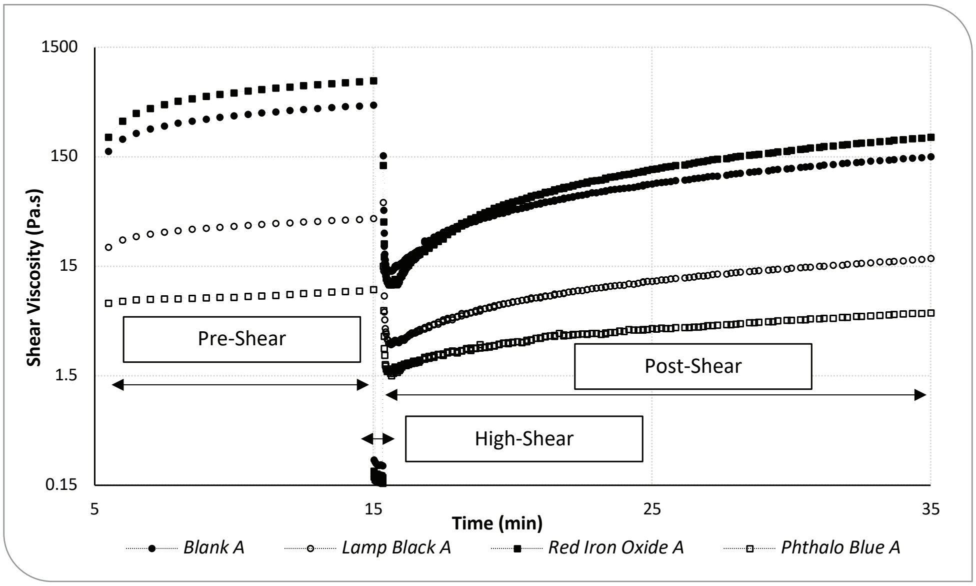


FIGURE 4 Time-dependent changes in viscosity during the 3-ITT of the HEUR A formulations.

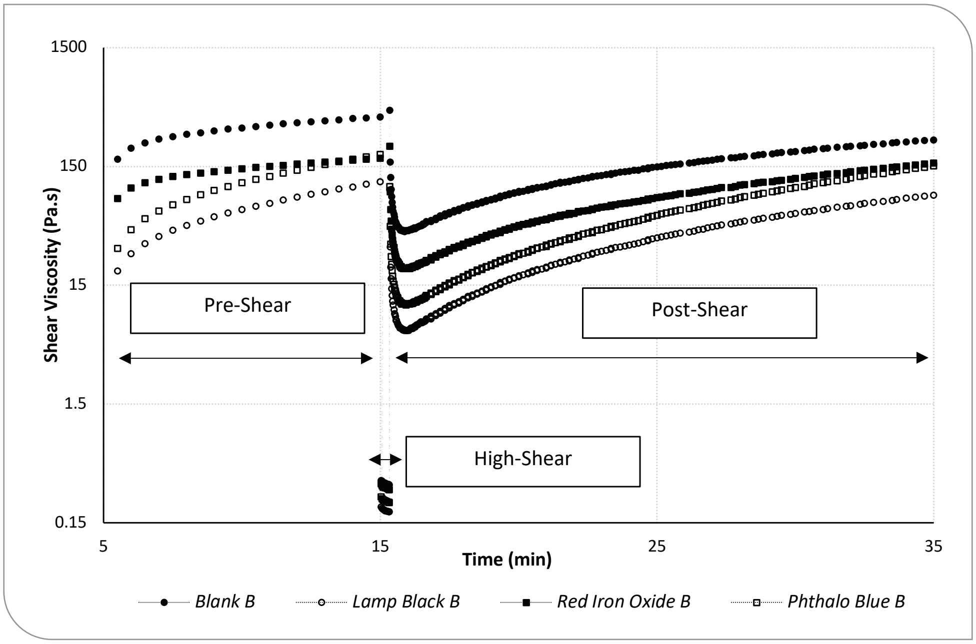
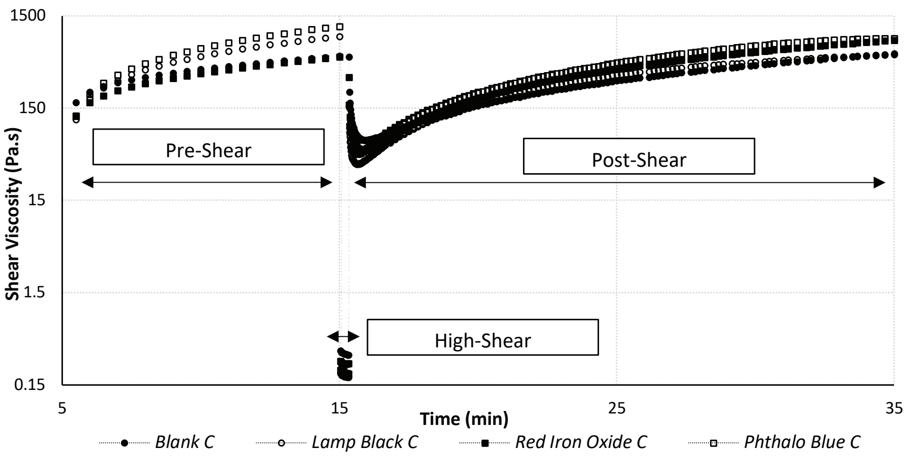


FIGURE 5 Time-dependent changes in viscosity during the 3-ITT of the MFC B formulations.

FIGURE 6
Time-dependent changes in viscosity during the 3-ITT of the MFC C formulations.



To show the stabilizing effect of MFC on the tinted formulations, an analysis was done on the high-shear and low-shear viscosity values for each formulation analyzed **(Table 2).** Using the raw data from the 3-ITT curves for each formulation in **Figures 4, 5, and 6,** the percentage difference (%) between each final high-shear viscosity value (Pa.s) and the lowest post-shear viscosity value (Pa.s) was calculated. An example of the percentage difference calculation for the *"Untinted A"* formulation is shown below:

Viscosity Change -> 14 – 0.23 = 13.8 Pa.s,
Average Viscosity -> (0.23 + 14)/2 = 7.1 Pa.s
Percentage Difference -> (13.8/7.1) x 100 = 193.5%

Using the percentage difference values, the variance value (%[2]) was determined to show the magnitude of deviation for each type of formulation based on universal colorants used. This value indicates the variability in viscosity for each type of formulation analyzed. The smaller the variance value the smaller the variability in the viscosity. The overall results are shown in **Table 2.**

As shown in **Table 2**, the use of the HEUR shows a greater difference in the variance of the formulations when different tinting additives are used (93.6 %[2]). However, when MFC is utilized instead of the HEUR technology, the variance decreases dramatically and is almost zero for the MFC C formulation (0.02 %[2]). In a practical sense, this means that directly after application onto a surface, either by roller or by spraying, the variations in viscosity are less noticeable with the MFC-based formulations. Indeed, at the highest level of MFC dosage (MFC C), there will be negligible differences in viscosity development after application, regardless of the universal colorant used.

This stabilizing phenomenon, as discussed earlier, can be explained by the thickening mechanism of MFC. The thickening is based on physical entanglement as well as on hydrogen bonding. Both mechanisms are not impacted by the addition of associative compounds, such as surfactants, commonly present in the universal colorants. In addition, changes in temperature or pH[5] do not have any impact to the viscosity of MFC. An example of the heat stability in **Figure** 7 is shown by the complex viscosity (Pa) stability of a 1 wt % aqueous MFC suspension at varying temperatures (10-90 °C).

Effect of MFC on the Acrylic Satin Paint Formulation

The ability of MFC to prevent viscosity loss on tinting was studied further with an acrylic satin formulation **(Table 3).** The formulation was based on an acrylic binder, with either a non-ionic low-shear thickening HEUR thickener (Rheology Modifier 1), specifically designed for preventing the loss in viscosity upon tinting or MFC as a multifunctional additive. In both cases, HEUR thickeners (Rheology Modifiers 2 and 3)

TABLE 2
Variance of the Formulations under 3-ITT Testing

Formulation	Final High-Shear Viscosity Value (Pa.s)	Lowest Post-Shear Viscosity Value (Pa.s)	Percentage Difference (%)	Variance (%²)
Untinted A	0.23	14	193.5	93.6
Lamp Black A	0.16	3	179.7	
Red Iron Oxide A	0.18	10	192.9	
Phthalo Blue A	0.16	2	170.4	
Untinted B	0.32	43	197.0	10.9
Carbon Black B	0.18	6	188.3	
Iron Oxide B	0.25	21	195.3	
Phthalo Blue B	0.2	10	192.2	
Untinted C	0.31	66	198.1	0.02
Carbon Black C	0.18	37	198.1	
Iron Oxide C	0.29	53	197.8	
Phthalo Blue C	0.22	47	198.1	

FIGURE 7
Temperature stability of MFC (1 wt % aqueous suspension).

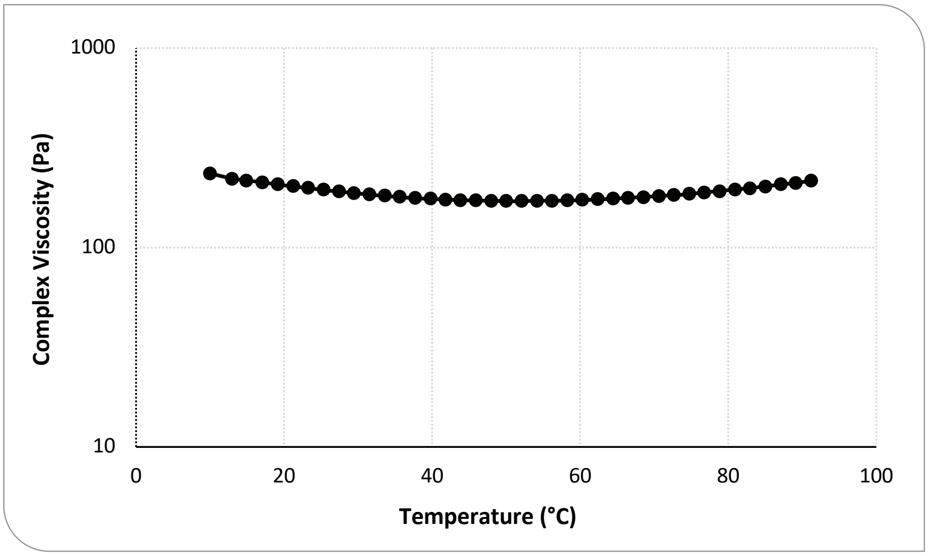


TABLE 3
Acrylic Deep Base Formulations

Components	HEUR A	MFC B	MFC C	MFC D
	wt %	wt %	wt %	wt%
Water	16.0	16.0	16.0	16.0
pH Modifier	0.1	0.1	0.1	0.1
MFC *(Biobased Rheology Modifier)*	-	2.0	3.0	4.0
Co-Solvent	1.1	1.1	1.1	1.1
Defoamer	0.3	0.3	0.3	0.3
Dispersant	0.2	0.2	0.2	0.2
Surfactant	0.4	0.4	0.4	0.4
Preservative	0.3	0.3	0.3	0.3
Filler	2.7	2.7	2.7	2.7
Titanium Dioxide Pigment	8.0	8.0	8.0	8.0
Attapulgite Clay *(Thixotropic Thickener)*	0.3	0.3	0.3	0.3
Binder *(Anionic Acrylic Co-Polymer Dispersion)*	51.2	51.2	51.2	51.2
Defoamer	0.3	0.3	0.3	0.3
Water	9.8	9.8	9.8	9.8
Coalescing Agent	0.5	0.5	0.5	0.5
Rheology Modifier 1 *(Non-Ionic Low-Shear Thickening HEUR)*	1.9	–	–	–
Rheology Modifier 2 *(Non-Ionic High-Shear Thickening HEUR)*	2.8	2.8	2.8	2.8
Rheology Modifier 3 *(Non-Ionic Mid-Shear Thickening HEUR)*	0.9	1.9	1.7	1.4
Water	3.2	2.1	1.3	0.6
Total (wt %)	**100.0**	**100.0**	**100.0**	**100.0**

were also used to adjust the mid- and high-shear viscosities. The base paint was tinted (8 oz/gal) with the same three colorants as for the formulations in **Table 1.**

The formulations in **Table 3,** were analyzed for KU viscosities, sag resistance, flow/leveling, and the effect on gloss.

Figure 8 shows the KU viscosities for all finished formulations before and after tinting. Addition of the colorants into the untinted formulations causes a drop in the KU values of approximately 15-20%.

Comparing KU values for the HEUR A formulations with the MFC formulations, there is a slight increase in viscosity at the highest dosage of MFC (MFC D), but no dramatic change. This means that there will be no significant difference to the in-can viscosity of the final formulations if MFC is used instead of the HEUR.

The sag resistance and flow/leveling properties of each of the formulations in **Table 3** were measured and the data is shown in **Figure 9.** There is a noticeable increase in sag resistance when MFC is utilized instead of the HEUR, especially at the higher dosages (MFC C and MFC D). There is also a consistency to the level of sag resistance measured when MFC is used as a thickener together with a colorant. There is very little change in sag resistance (≤ 2 mils) across all colorants used regardless of the level of MFC dosage. The consistency in these sag-resistance values also reinforces the low level of variance seen with the data shown in **Table 2.**

FIGURE 8
KU viscosities of the untinted and tinted (Lamp Black, Red Iron Oxide, Phthalo Blue) formulations.

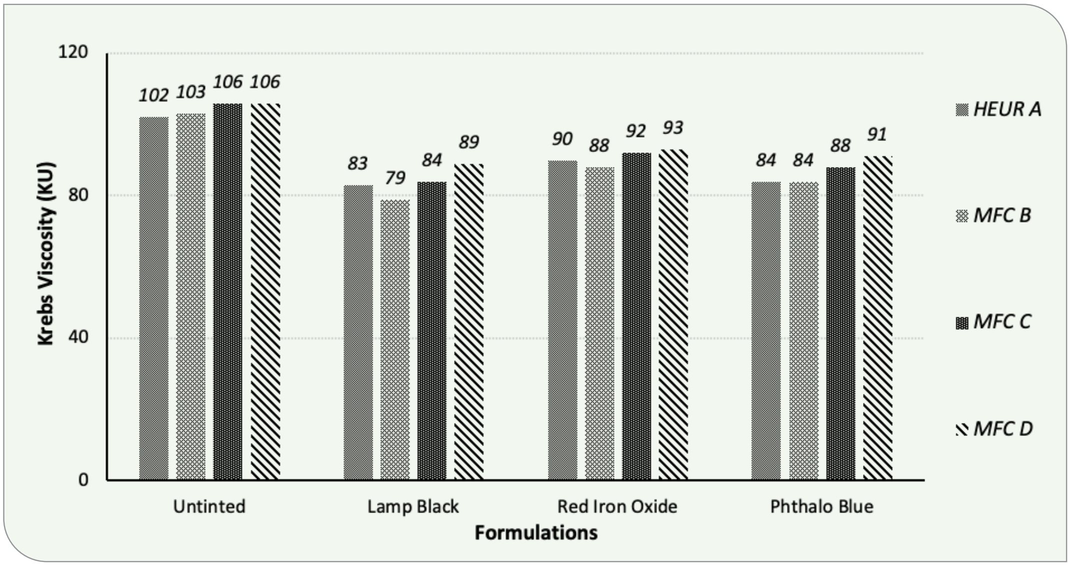


FIGURE 9
Sag resistance and leveling of the untinted and tinted formulations.

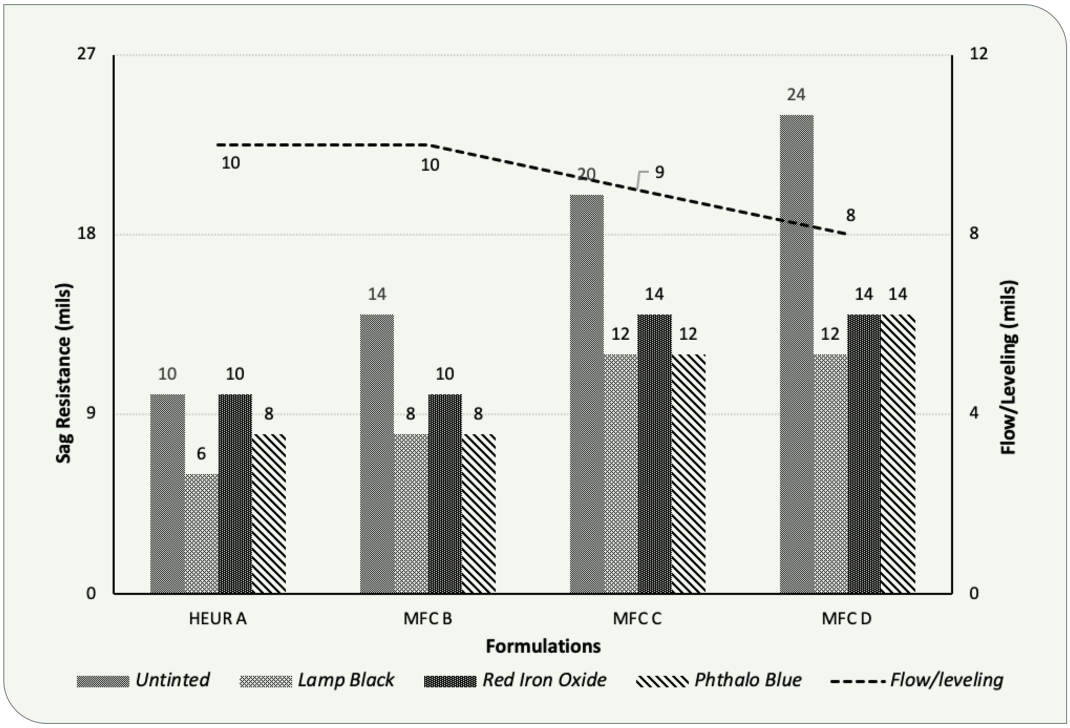
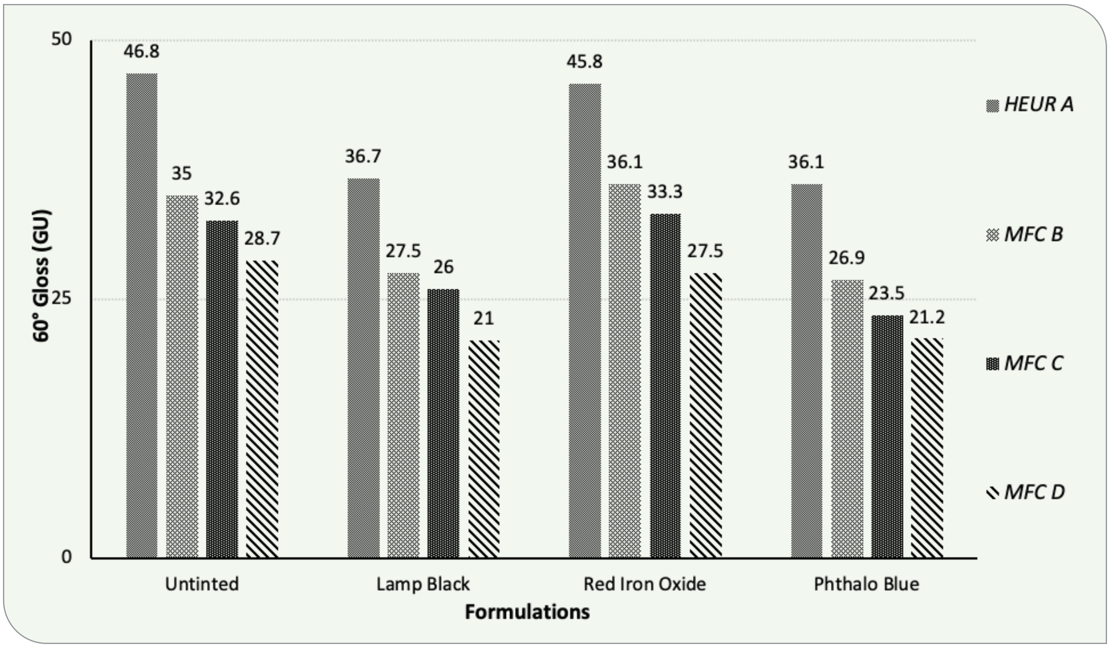


FIGURE 10
Gloss values for the untinted and tinted formulations.



However, there is a noticeable drop in sag resistance when a colorant is used with MFC. This is most likely due to the HEUR interacting with the colorant technologies reducing with interaction with the MFC. This leads to a drop in the sag-resistance values, but they are still higher than the reference values. The interaction of the HEUR with the colorant breaks the bonding present between the HEUR and MFC fibrils, and in turn, reduces the sag-resistance values in **Figure 9**.

The flow/leveling values (mils), illustrated by the dotted line, are the actual values for all the formulations tested either as untinted or with the various universal colorants. The flow/leveling values are maintained regardless of whether the HEUR or MFC is used as a thickener. Moreover, the use of MFC increases the sag resistance of a formulation while maintaining the flow/leveling properties. This reinforces the unique property of MFC imparting exceptional sag resistance while preserving the flow/leveling properties, even when universal colorants are used.

The gloss values (GU), measured at 60°, for both the untinted and tinted formulations, containing both HEUR and MFC, are shown in **Figure 10.** The formulations containing the HEUR technology have a loss in gloss with the organic universal colorants (Lamp Black and Phthalo Blue), while the inorganic Red Iron Oxide universal colorant gloss value is maintained. Substitution of the HEUR technology with MFC causes the 60° gloss values to decrease across all formulations tested. This is due to the mattifying effect that MFC exhibits when added into coatings formulations, which is mainly due to the increase in the surface roughness of the coating. The increase in the surface roughness is potentially due to the inhomgeneity of the fibrils of the MFC forming large fibril aggregates. These aggregates can lead to an inhomgenous fibril distribution within the coating leading to increased surface roughness, in-turn reducing the gloss value.[6]

Conclusion

The effect of MFC on the rheology of the coating formulations is striking. MFC effectively prevents the viscosity loss after tinting compared to current technologies. The high viscosity at rest, combined with high yield stress, results in stable formulations, and allows homogenous formulations even in the presence of heavy particles or low-density fillers. In addition, the high viscosity at rest enables increased applied film thickness, thereby reducing the number of applied film layers required, without comprising the final coating properties. The relatively fast viscosity recovery leads to excellent sag resistance without sacrificing the leveling of the coating.

Depending on the dosage of MFC, effects on the gloss of the coating can be seen. This opens possibilities to formulate smooth-surface flat paints. MFC is a sustainable, renewable, and VOC-free multifunctional additive, which cannot only replace synthetic additives in formulation, but also contributes added value to the end products. ❊

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