

THE IMPACT OF RHEOLOGY MODIFIERS ON THE VISCOSITY OF DECORATIVE WATER BASED PAINT UPON TINTING

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Lucrarea prezintă analiza influenței modificatorilor reologici (de tip HASE - polimer anionic și HEUR - polimer neionic) asupra vâscozității unei vopsele decorative pe bază de apă în urma colorării acesteia în prezența polimerului neionic celulozic modificat (de tip HEC și HMHEC). Sistemele de colorare folosite în această lucrare sunt sisteme universale (albastru ftalo, oxid roșu de fier și negru de fum), dispersii de pigmenți și surfactanți, cu un impact major asupra performanțelor produsului final. Combinația optimă acționează printr-un mecanism ce are ca scop furnizarea a trei proprietăți dorite pentru vopselele colorate: îmbunătățirea rezistenței la scăderea vâscozității, menținerea unei bune fluidități și îmbunătățirea rezistenței la scurgere. Aceste trei proprietăți sunt redată prin măsurători ale vâscozității Stormer (KU) înainte de colorare, după colorare și la un timp după depozitarea vopselei și depind de aplicare (pensulă, rolă, procedură "air-less") dar și de calitatea filmului de vopsea aplicată, după uscare.

This paper presents the influence of the rheology modifiers (HASE type - anionic polymers and HEUR type - non-ionic polymers) on the viscosity of water-based decorative paints after tinting in presence of non-ionic modified cellulosic polymer (HEC and HMHEC types). Tinting systems used in this work are common systems (Blue Ftalo, Iron Red Oxide and Lampblack), dispersions of pigments and surfactants, with a major impact on the final product performance. The optimal combination aims to provide three desired properties for tinted paints: improved resistance to viscosity loss, an excellent flow and improved sag resistance. These three properties are evaluated by measurements of Stormer viscosity (KU) before tinting, after tinting and after paint storage and depend on the application method (brush, roller, air-less) and also by the quality of the dry film paint applied.

Keywords: rheology modifiers, viscosity, water based paints, associative thickeners, surfactant, tinted paints

1. Introduction

A latex paint formulation requires careful adjustment of the rheology. The interaction/association between the ingredients of a typical paint formulation

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coating rheology systems, the balance between ingredients (such as binder, pigments, solvents, dispersants and surfactants) can not be ignored in order to develop coating rheology systems [1].

A latex paint requires the addition of thickeners to achieve the desired rheological behavior. The thickeners are water soluble polymers such as cellulose derivatives, non-ionic - hydroxyethyl cellulose (HEC) or their derivatives - hydroxymethyl hydroxyethyl cellulose (HMHEC), of high molecular weight [2-7].

As compare with traditional powder thickeners (like conventional HEC type or the mineral ones), the synthetic thickeners are liquid associative polymers called rheology modifiers that ensure easier usability due to their liquid state [8].

These rheology modifiers may be synthetic non-ionic polymers like hydrophobe-modified ethoxylate urethanes type (HEUR) and anionic polymers like polyacrylic acids, alkali-swelling/soluble emulsions type (ASE) or their hydrophobe-modified type (HASE) [9].

The choice and combination of these modifiers are reflected on the rheological properties of the liquid in can (sedimentation, decrease viscosity on water dilution or on tinting, flow and leveling, spattering resistance) and on the paint film properties depending on its destination: indoor (gloss development, scrubability, hiding power, stain resistance and stain removal, color compatibility and tint strength) and outdoor (dirt pickup, adhesion and blister resistance, efflorescence, corrosion resistance, mildew resistance, grain crack resistance). The important features of rheology are highlighted by the methods of application: brush - flow and leveling, open working time, drip resistance, roll – spatter-free, flow and leveling, spray - good atomization [10].

The thickening mechanism and the interactions of the rheology modifiers with various surfactants have been extensively discussed and analyzed [11-12], demonstrating the impact they have on the systems properties, ensuring the desired performance. The behavior of HASE polymer model in solutions has been clearly explained in many other works, showing its role in a solution due to the chemical structure but also to the network which it forms after neutralization. Investigation of cellulose by various mechanical analyses and immobilization of compounds on cellulose media were the basis of extensive works proving the importance and significance of the cellulose in a film-forming system [13].

Nowadays the architectural coatings market is governed by color. The paint industry is progressively trying to avoid the use of solvent-based coatings for environmental and health and safety considerations. The trends are evident and today's homes are increasingly painted with deep, vibrant colors, both inside and outside. These shades require the use of considerable amounts of colorants, organic and/or inorganic. The colorants (surfactant/ pigment blends) have a major impact on the performance characteristics of the final coating paint and perhaps

the most notable change is the reduction in viscosity observed on tinting especially when associative thickeners are employed [14].

The goal of this study is to analyze the influence of the rheology modifiers (non-ionic: HEUR and anionic: HASE) on the viscosity of water-based decorative paints and their importance on the quality of the final paint in the presence of cellulosic thickener as HEC / HMHEC.

2. Experimental

The materials and the recipes used in this study are presented in Table 1.

Table 1

The basic transparent bases recipes of styrene-acrylic latex based semi-gloss emulsion

Ingredients / Steps	Composition, %				Chemical composition
	Sample 1	Sample 2	Sample 3	Sample 4	
1. Preparing the paste					
Water	46.71	46.86	46.79	46.67	
Thickeners (HEC)	0.9	0.9	0	0	medium molecular weight hydroxyethyl cellulose, with a viscosity range 1100-1500 cP, sol 1%, Brookfield viscosity
Thickeners (HMHEC)	0	0	0.7	0.7	hydrophobically modified hydroxyethyl cellulose, with a viscosity range 1300-1800 cP, sol 1%, Brookfield viscosity
Dispersing agent	0.45	0.45	0.45	0.45	sodium polyacrylate agent
Wetting agent	0.3	0.3	0.3	0.3	non-ionic wetting agent
Biocide	0.3	0.3	0.3	0.3	5-chloro-2-methyl-4-isothiazolin-3-one
Foaming agent	0.44	0.44	0.44	0.44	mineral oil
Anti-frost agent	0.5	0.5	0.5	0.5	glycol agent
Neutralizing agent	0.1	0.1	0.1	0.1	aminomethyl propanol
Fillers	22	22	22	22	calcium carbonate, calcined kaolin clay
2. Completing					

the paste					
Surfactant	0.6	0.6	0.6	0.6	quatarnary ammonium compound
Latex	26	26	26	26	styrene-acrylic, 50%
Coalescent agent	1.2	1.2	1.2	1.2	2,2,4-Trimethyl-1,3-pentenediolmono(2-methylpropanoate)
3. Rheological Control					
HASE	0.5	0	0.62	0	hydrophobically modified alkali soluble emulsions
HEUR	0	0.35	0	0.74	hydrophobically modified ethoxylated urethane emulsions
TOTAL	100.00	100.00	100.00	100.00	

The features of these recipes are:

PVC = 30 %;

NVW = 50 %;

NVV = 35 %.

Abbreviations:

HEC = medium molecular weight hydroxyethyl cellulose, with a viscosity range 1100-1500 cP, sol 1%, Brookfield viscosity

HMHEC = hydrophobically modified hydroxyethyl cellulose, with a viscosity range 1300-1800 cP, sol 1%, Brookfield viscosity

HASE = hydrophobically modified alkali-soluble emulsions

HEUR = hydrophobically modified ethoxylated urethane emulsions

PVC = pigment volume concentration

NVW = non-volatile weight

NVV = non-volatile volume

Procedure for obtaining paints: 1. Obtaining pigment grind - dispersion of a HEC thickener in water using a Cowles type mixer to a high speed -1200 rpm-for 25 min, adding other ingredients. Pigment grind fineness: max. 40 microns.
2. Completion of pigment grind - adding the coalescent agent and styrene acrylic latex resin at a low mixing speed- 800 rpm.

3. Rheological control - adding rheology modifiers HASE/HEUR at a low mixing speed; always dissolve in a minimum amount of water, in a ratio of 1:1 to avoid forming agglomerations.

The parameters studied in this work and the analysis methods usually used employed are presented in Table 2.

Table 2

Analysis methods	
Parameters	Details of test method
Fineness of grind gages	ASTM D 1210, a higher number indicates a finer size of particles
STORMER viscosity	ASTM D 562, a higher number indicates a higher viscosity of the paint in the container
BROOKFIELD viscosity	ASTM D 1131, a higher number indicates a higher viscosity of the paint in the container
ICI viscosity	ASTM D 4287, a higher viscosity (at 12000 s-1) indicates a higher load of the brush, and the forming of a better film
Water resistance test	ISO 11998, a greater loss upon washing of the dry film thickness applied at the same number of cycles, indicating a weaker resistance to water
Spattering resistance	ASTM D 4707, a higher number indicates greater resistance to spattering
Flow resistance	ASTM D 4400, a higher number indicates greater resistance to flow
Leveling appearance	ASTM D 4062, a higher number indicates a better smoothing of the paint film
Sag resistance	ASTM D 4400, a higher number indicates a better sagging of the paint film
Storage stability	ASTM D 1849, 4 weeks at 48 °C
Color acceptance	Pre-dispersion of the colorant in mono-propylene-glycol was added in a percentage of 5 %

The recipes are representative for deep shades bases, without content of titanium dioxide, also known as transparent bases, in order to assess the major impact on viscosity after tinting. These bases contain styrene-acrylic latex for interior destination. The colorants (Blue Ftaló, Iron Red Oxide and Lampblack, dispersed in a large amount of surfactants) are universal and are dispersed throughout the obtained bases using disperser-Dispermat, at an average speed of 600-700 rpm.

The proposed variants are rendered in the laboratory disperser- Dispermat, using a minimum amount of 3 kg for each variant, keeping the same weighing errors (the same electronic scale), the same batches of raw materials, the same technology and to the same order in placing the raw materials, the same homogenization time, all performed by the same worker. The variants obtained are stored in the identical conditions of temperature and humidity in the laboratory ($20 \pm 3^{\circ}\text{C}$, 50%), and analyzed in terms of their characteristics after 24 hours as of preparation. Analysis of these variants will be made by the same worker in the same working conditions to eliminate as many errors as possible.

Sagging measurements of the liquid paint were made using a graduated metal applicator which applies the paint on a white-black card and then the card is positioned vertically. Then the gradation values of the sagging paint are read.

3. Results and discussion

The influence of two types of modified cellulose (HEC and HMHEC) with about the same viscosity and two rheology modifiers (HASE and HEUR) was studied. The ratio between them will be chosen so at the final all four bases have the same physicochemical characteristics measured by Brookfield, Stormer, ICI viscometers, in order to not penalize them after tinting. The obtained values of viscosity are presented in Table 3.

Table 3

Bases characteristics before tinting				
	Values / Samples			
	1	2	3	4
Brookfield viscosity, R 5, 30 rpm, cP	7500	8200	7900	8000
Stormer viscosity, KU	108	110	110	114
ICI viscosity, P	1.58	1.68	1.65	1.68

As a preliminary tinting test we made a dilution of all four bases, 10% dilution with water (maximum recommended dilution for the first coat of white paint and / or color paint); the new values of viscosity measured at 24 hours after dilution, with above three instruments (Brookfield, Stormer-KU, Cone & Plate-ICI) are shown in Table 4.

Table 4

Bases characteristics after 10% dilution with water before tinting				
	Values / Samples			
	1	2	3	4
Brookfield viscosity, R5, 30 rpm, cP	7100	8000	6900	7900
Stormer viscosity, KU	96	105	88	103
ICI viscosity, P	1.38	1.50	1.46	1.53

Note that upon dilution of 10% water, which is recommending as the maximum dilution required for the first layer of both white and colored paint, transparent bases have been modified, especially regarding KU viscosity for Sample 3, which means that after tinting, the obtained values will drop down even more due to the influence of colorant surfactant, that are more aggressive than water.

The effect of decreasing viscosity of the bases on tinting is revealed using three specific colorants: Iron Red Oxide, Lampblack and Blue Ftalo, added at a rate of 5% each over each base. This percentage represents the fill factor compared to a liter of paint, that is the ratio tint: transparent coloring- colorants.

The Samples 1 and 2, which are the most stable in terms of rheological appearance, are still colored with 5% of Lampblack and 5% with Blue Ftalo. The main and the most relevant feature in this study is the Stormer viscosity, which represents the most accurate the dropping viscosity on tinting. Thus, the Stormer loss viscosity for the two samples after tinting is shown in Fig. 1.

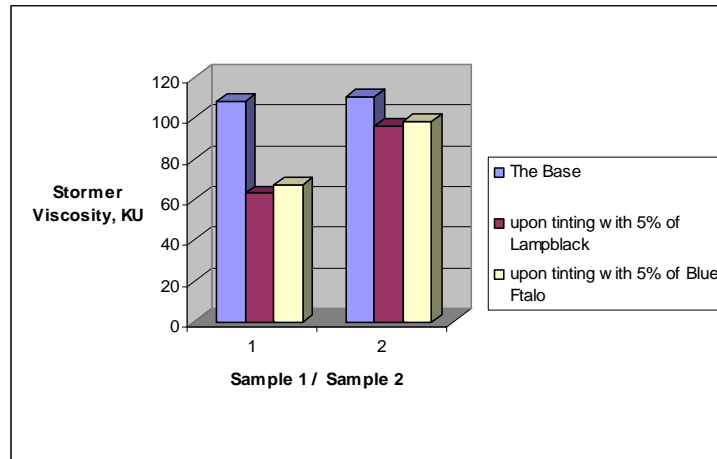


Fig. 1. Loss Stormer viscosity for Sample 1 and Sample 2 upon tinting

Fig. 1 illustrates that the Sample 2 which contains a non-ionic rheology modifier is much stable upon tinting than Sample 1 which contains anionic rheology modifier. However, the Sample 1 can be improved if 60% of the HASE content is replaced with an HEUR. The values of the viscosities are situated between those of Sample 1 and Sample 2. This new obtained sample, Sample 5, presents after tinting an improvement in loss of viscosity than Sample 1; the comparison between these two samples is shown in Fig. 2.

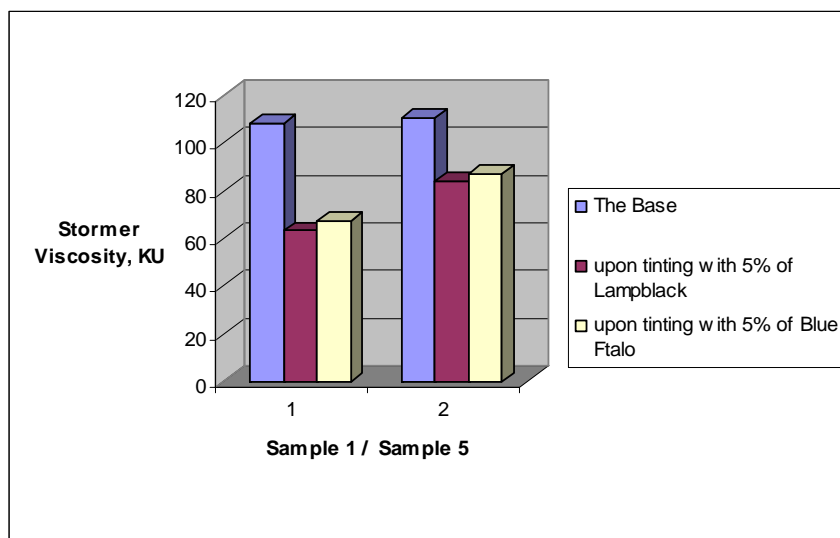


Fig. 2. Improvement loss Stormer viscosity for Sample 1

However, the above replacement does not solve all the problems that HASE brings to the system, even if it is in a small proportion. The difficulties are related to a low pH which may shock the system and cause stability problems; also the issues with water sensitivity of HASE products can limit their use in areas such as bathrooms, kitchens and on exterior applications. Fig. 3 illustrates the viscosity drop upon tinting for Sample 3.

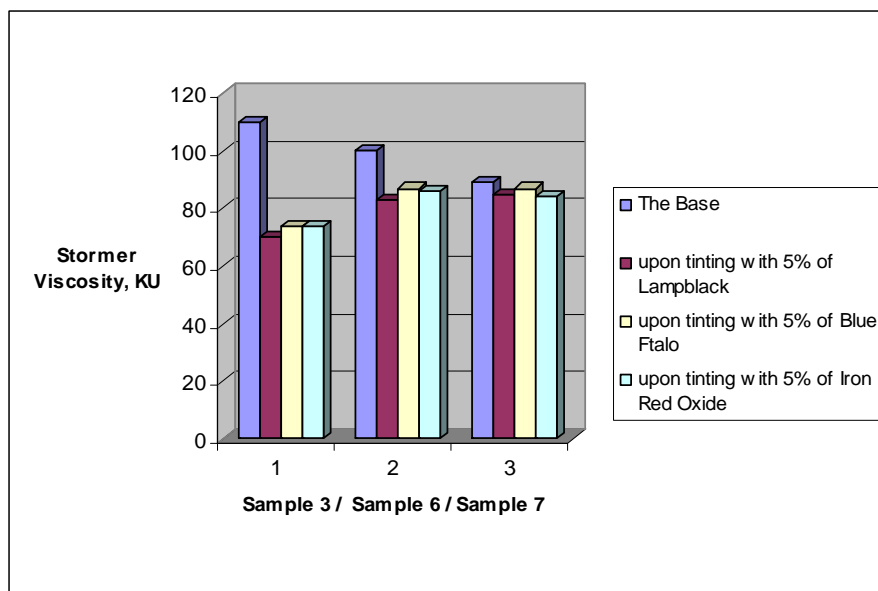


Fig. 3. Loss Stormer viscosity upon tinting for Sample 3 and improvement loss Stormer viscosity for it

The Sample 3 shows a decrease in Stormer viscosity after tinting; however, by replacing 60% and 75% of the HASE with HEUR (obtained Sample 6 and Sample 7), an improving of the Stormer viscosity loss was noticed.

A stable viscosity is achieved through the networks formed between latex particles and the interactions that contribute to the network strength. These interactions are formed of thickeners adsorbed on the latex surface; these interactions form high shear zones (also known as ICI areas) and mid shear zones (zones called KU). The amount of ICI zones is higher than the number of KU zones adsorbed on the latex surface. Only HEUR lower molecular weight structures than those of the thickeners in the high shear areas is not recommended. This difference in molecular weight generates different volumes of space occupied by the two components when adsorbed on the latex surface, thus hindering HEUR access to the lower molecular weights compounds. This steric crowding makes some of the hydrophobic group from HEUR polymer inaccessible for network building and inactivates a fraction of these thickener polymers.

When colorants are added, the surfactants will displace both ICI and KU areas from the latex surface, this change resulting in a decrease of the steric crowding at the surface. This fact allows the inaccessible chains to participate in network building. The colorant activates the mechanism which increases viscosity upon the addition of surfactant and lowers the base viscosity upon tinting.

Because HEC in comparison with HMHEC shows excellent properties of color acceptance, better spattering resistance and reduce the gloss, HEC is preferable to be used for indoor destination.

Another important property of these combinations, HEC / HASE-HEUR, is a good sag resistance for paint film when it is applied on the vertical support. The values read with the graduated applicator are shown in Fig. 4.

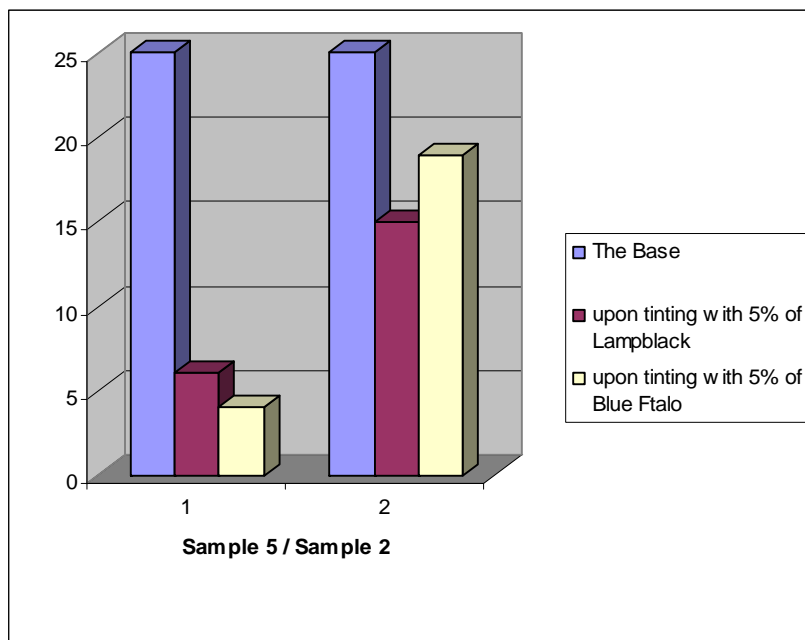


Fig. 4. Sag resistance comparison between Sample 5 and Sample 2

Fig. 4 clearly shows that a combination of HEC/HEUR as in Sample 2 leads to a better sag resistance of paint film in comparison with the HEC/HASE-HEUR combination as in Sample 5.

The storage stability for Sample 2 was followed by conditioning it for four weeks at 48⁰ C, and then Sample 2 was re-analyzed by measuring the viscosities. The obtained values are shown in Fig. 5.

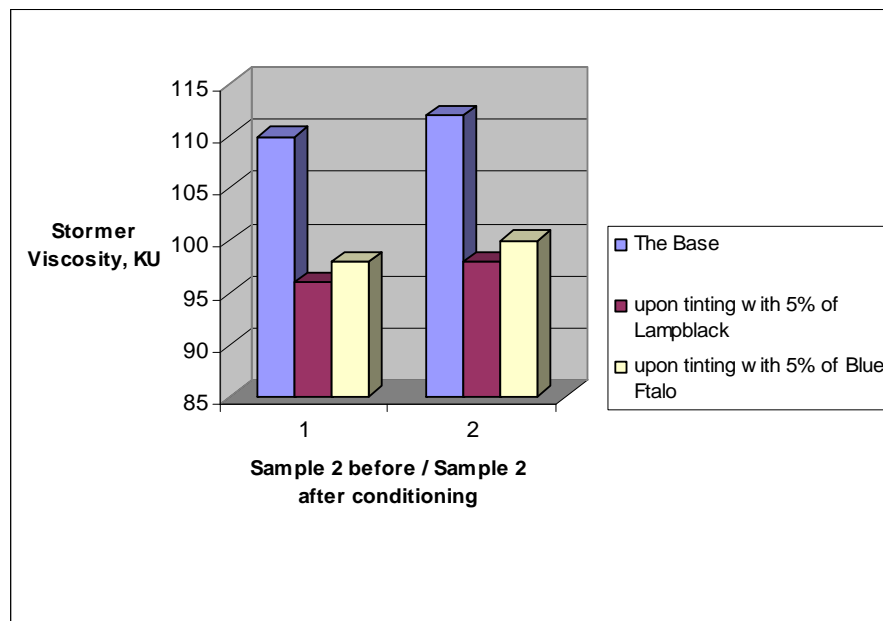


Fig. 5. Stormer viscosity comparison for Sample 2, before and after conditioning

After conditioning, the liquid Sample 2 does not present pigment separations above and after drawn them down on the white-black cards and any migrations of pigment were not noticed by the rub-out test.

Rheology modifiers (HASE/HEUR) are associative polymers, water soluble compounds which contain two or more hydrophobic groups. These hydrophobic groups associate with the hydrophobic groups of modified rheological polymers and also with latex particles and form a network which determines an increased viscosity. The colorants, especially the commercial ones, contain high concentrations of surfactants.

The hydrophobic groups of the surfactants are adsorbed on the latex surface substituting rheology modifiers from the surface. This process results in fewer hydrophobic groups and weaker network and thus a lower viscosity. The surfactants will break the associations between rheology modifiers which lowers the viscosity. This The effect can be avoided by replacing the associative modifiers with non-associative modifiers.

This replacement however will be accompanied by a poor flow of the final product, a consequence of the flocculation determined by the non-associative modifiers. The effect of the flocculation process is an increased viscosity at low shear force, reflected in a poor flow and leveling of the paint film. Another way to avoid the decrease in viscosity upon tinting is to over thicken the un-tinted base paint, so that after tinting, the viscosity drops to the desired final viscosity. This

leads to a high cost for the final formulation and makes handling and packaging very difficult during production. Therefore, the best solution nowadays when the colored paint market continues to grow, is finding the rheology modifier that offers good stability paint upon tinting. Thus, this rheology modifier is a HEUR type, non-ionic; together with a HEC the HEUR modifier, can provide a stable viscosity upon tinting, and also excellent flow and leveling properties of the paint film, odorless for being in agreement with current and future on VOCs regulations.

2. Conclusions

Sample 2 which contains a non-ionic rheology modifier is much stable upon tinting than Sample 1 which contains anionic rheology modifier. The combination of HEC/HEUR leads to a better sag resistance of paint film in comparison with the HEC/HASE-HEUR combination.

Using a combination between a cellulosic thickener of HEC type and a rheology modifier of HEUR type, non-ionic, a new mechanism to provide three desired properties for the tinted paints allows to have:

- a significant improvement of the resistance to viscosity loss;
- improved sag resistance tinted paint applied on the vertical support;
- allows the existence of an appropriate thixotropic flow even after storage.

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