The Influence of Rheology Modifiers and Dispersing Agents on the Quality of Water-based Decorative Paints

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The purpose of this paper is to analyze the influence of dispersing agents (polyphosphate and polyacrylate types) but also of rheology modifiers (HASE and HEUR types) using the same medium molecular weight cellulosic polymer (HEC type) and an acrylic emulsion. The analyzed parameters are strictly related to the role and influence of these raw materials in the system but also to their concentration in the formulation of the paint chosen. These variables and the quantities used are selected depending on the final parameters set (storage stability, water resistance, hardness, UV resistance, hiding power, flow, leveling, etc.).

Keywords: water based paints, rheology modifiers, dispersing agents, VOC

Water-based synthetic rheology modifiers consist of multi-compatible solutions for formulations, reducing the viscosity of the medium (dispersion agents) or improving their rheological profile (thickeners). Due to the excellent properties that these agents have the solutions provide benefits from manufacturing to paint application.

Rheology modifiers can be classified as natural or synthetic derivatives. Three general classes based on synthetic acrylic polymers comprise a group of products used as rheology modifiers in various applications. The first class is based on acrylic acid homopolymers and copolymers, their esters and maleic acid. This group includes alkali-soluble emulsions (ASE). Modification of this group by adding hydrophobic polymers leads to the second category of synthetic rheology modifiers known as hydrophobically modified alkali-soluble emulsions (HASE). This group of polymers, more frequently used as associative thickener offers greater control over compound rheology than ASE. The third category of synthetic rheology modifiers consists of hydrophobically modified ethoxylated urethane resins (HEUR). This group of polymers usually consists of polyethylene glycol units with different molecular weights, joined by urethane links and ending with hydrophobic groups. Unlike ASE and HASE classes, HEUR rheology modifiers are nonionic substances and their effect does not depend on the alkalinity to activate the thickening effect [1-3].

As compared to traditional powder thickeners, such as the conventional HEC type or the mineral ones, the liquid rheology modifiers ensure easier use due to liquid form. Water-based synthetic rheology modifiers are positioned at the highest level of performance to ensure a formulation with a viscosity obtained at any shear rate.

The thickening mechanism and the interactions of such rheology modifiers with various surfactants have been extensively discussed and analyzed [4], showing the impact they have on the properties of systems and ensuring the achievement of the desired final performance. The behavior of HASE polymer model in solutions has been clearly explained in many other works, showing their 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 demonstrating the importance and significance of the cellulose in a film-forming system [5-6].

The rheology of hydrophobically modified ethoxylated urethanes (HEUR) and their interaction with surfactants served as basis for other studies carried out for explaining their functions and the interaction with the aqueous system. The results confirm that rheology additives help to increase their viscosity due to network formed and to the final hydrophobic groups existing in their chemical structure [7-8].

This paper aims at demonstrating the role of each rheology modifier but also of dispersing agents and their influence and importance on the quality of a water-based paint, all of them being reflected in the measurements specific to the set parameters.

Materials and devices

The materials and the recipe used in this study are presented in table 1. The recipe to be considered is a basic recipe for a semi-gloss emulsion paint based on acrylic latex, which shall be subjected to various studies by the variation of raw materials analyzed by this study.

Procedure for obtaining paints

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.

Completion of pigment grind - adding the coalescent agent and acrylic latex resin at a low mixing speed- 800 rpm.

Rheological control - adding the modifier or rheology modifiers 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 are presented in table 2.

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Table 1
THE BASIC RECIPE OF ACRYLIC LATEX BASED SEMI-GLOSS EMULSION

Ingredients / Steps	Composition %	Chemical composition
1. Preparing the paste		
Solvent	11.88	Water
Thickeners (HEC)	0.40	Hydroxyethyl cellulose
Dispersing agent	0.6	Nonionic wetting agent
Biocide	0.2	5-Chloro-2-Methyl-4-Isothiazolin-3-One
Foaming agent	1.4	Mineral oil
Anti-frost agent	2.15	Glycol agent
Neutralizing agent	0.2	Aminomethyl propanol
White pigment	19	Titanium dioxide
Filler	10	Natural calcium carbonate
2. Completing the paste		
Surfactant	0.6	Quaternary ammonium compound
Latex	47	Acrylic, 50%
Coalescent agent	6.07	Propionic acid, 2-methyl, monoester with 2,2,4-trimethyl-1,3-pentandiol
3. Rheological Control		
Rheology modifiers (HASE, HEUR)	0.5	Acrylic, polyurethane agents
TOTAL	**100.00**	

The features of this basic recipe are:
PVC = 30 %
NVW = 50 %
NVV = 39 %

Abbreviations:
HEC = medium molecular weight Hydroxyethyl Cellulose, with a viscosity range 1100-1500 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
PU = Polyurethane
VOC = Volatile Organic Compound content

Table 2
ANALYSIS METHODS

Parameters	Details of test method
Fineness of the paste	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
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
Storage stability	ASTM D 1849, 7 days at 25^0 C
Tinting strength	Pre-dispersion of the colorant in mono-propylene-glycol was added in a proportion of 2%

Experimental part

The variants that served as basis for this study were differentiated by HEC, HASE and HEUR components and by their concentration in the standard emulsion chosen (table 1) in order to determine their effects on the characteristics of the paints and they are presented in table 3.

Apparatus

A disperser with different speed levels was mainly used. The values of the three types of viscometers considered served as basis for this rheological control study.

Procedure

The proposed variants are rendered in the laboratory disperser- Dispermat, using a minimum amount of 1.5 kg

Table 3
VARIANTS STUDIED IN TERMS OF QUANTITIES AND TYPES OF RHEOLOGY MODIFIERS

	V 1	V 2	V 3	V 4	V 5
HEC	0.4	0.7	0.4	0.4	0.4
HASE	0	0	0.5	0	0.5
HEUR	0	0	0	0.5	0.5

Table 4
CHARACTERISTICS OF THE VARIANTS PREPARED

Parameters	Values / Variants				
	V 1	V 2	V 3	V 4	V 5
Brookfield viscosity, cP	5000	6300	7000	7800	9300
Stormer viscosity, KU	78	82	88	94	123
ICI viscosity, P	0.47	0.47	0.67	0.71	1.2
Sagging resistance	7	7	10	12	10
Flow resistance	poor	good	good	very good	good
Leveling	poor	poor	good	Very good	poor
Spattering resistance	yes	yes	good	no	no
Tinting strength	no	no	excellent	excellent	excellent
ICI, P viscosity, after tinting with 5% black colorant	0.38	0.37	0.61	0.69	1
COV, g/l	24	28	20	10	13
Wet scrub resistance, number of wash cycles	1650	2200	1900	4500	1870
Hiding power %	98.37	98.43	98.7	99.11	99.05

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 same conditions of temperature and humidity in the laboratory (20 ± 3^0 C, 50%), and analyzed in terms of their characteristics after 24 h as of preparation. Analysis of these variants will be made by the same worker in the same working conditions so as to eliminate as many errors as possible.

Results and studies of the parameters analyzed

The physico-chemical characteristics that reflect the strict rheological control of the five variants V1-V5 different only by the type and concentration of the rheology agent are presented in table 4.

Study of emulsion viscosity V1-V5 variants

The correct adjustment of the final viscosity is considered a critical point for any formulation, thereby ensuring optimum properties such as scratch resistance, flow and leveling, film appearance and lack of sedimentation.

The measurements specific to the consistency of the analyzed emulsions and to their stability over time are analyzed using three types of viscometers, each of them providing different information on the nature of these emulsions.

The studied variants were analyzed using Brookfield viscometer (cP) at a low shear rate. There was noticed that at a low viscosity (e.g. V1 without using a rheology modifier) the paint film presents problems of flow and leveling upon application these defects becoming more obvious after drying. There was also noticed that the low viscosity caused problems in filler depositing during storage, after 7 days at 25° C. Increasing cellulose ether content (HEC=hydroxyethyl cellulose) without adding any rheology modifier (V2) did not improve these qualities. As rheology modifiers were added (V3 with HASE and V4 with HEUR) an improvement of the paints obtained can be noticed, the high Brookfield viscosity leading to problems of application, flow and leveling. V4 variant with HEUR modifier is even better than that one with HASE modifier, meaning that the polyurethane modifier effect was much higher than the acrylic one in terms of flow and leveling problems. On the other hand, in the case of V5 variants using both types of rheology modifiers having a viscosity above the optimal limit, problems may reoccur in terms of film leveling and filler depositing during storage. The optimal value of this viscosity ranges 7000-8000 cP, V3 and V4 variants being included in this range.

The second measured viscosity is Stormer viscosity (also called Krebs Stormer) (KU) for all five variants obtained, at a medium shear rate, considered optimal for the range 90-110 KU. Because the values of V1 and V2 variants are below the minimum limit, they cause problems upon moving them from a container to another and have a fast flow.V5 variant is well above the upper limit creating flow problems because of the high viscosity. The gel appearance of the paint creates problems in terms of homogenization and incorporation of colorants. V3 and V4 variants are appropriate in this regard.

The third characteristic of the obtained variants is ICI (P) viscosity, determined at a high shear rate, giving information about the reaction of paints upon application. Optimum range is about 0.9-1.0 P. The first three variantsV1, V2, V3, being below the lower limit, indicate a degree of spattering upon application, therefore do not provide good hiding power being necessary to apply several layers for the same effect or quantity, leading to higher spreading rate. It is noticed that the lack of the rheology modifier creates this effect (V1 and V2) but by adding a V3 HASE modifier the appearance is significantly but not sufficiently improved meaning that this option (V3) should be adjusted to solve this issue. Adding a V4 HEUR modifier is not a solution for this problem and although V5 has an ICI value above the maximum optimal limit it does not create spattering problems upon application. This V5 variant can also be adjusted if it is applicable as white paint, if it will be tinted by including liquid colorants this value will be considered appropriate to avoid drop viscosity after adding colorants.

Compared with cellulose thickeners, the newtonian HEUR rheology modifiers contribute to increasing hiding power and it is possible to cover the surface imperfection by using acrylic rheology modifiers. The main advantage of conventional thickeners with high molecular weight is their use in low concentration which leads to cost saving. We avoided this disadvantage by using a thickener with a medium molecular weight and with a viscosity range 1100-1500 cP, sol 1%, Brookfield viscosity.

A less sharp effect of the viscosity can be obtained by using a lower molecular weight thickener as compared to high molecular weight thickeners so that the film appearance and the hiding power are improved. On the other hand the disadvantage is that in order to obtain a high Stormer viscosity a greater amount of thickener should be used, thus generating high costs.

Filler dispersion study

Another aspect of this study relates to the use but especially to the right choice of the dispersing agent necessary for a total dispersion of the filler and pigments, thus ensuring a better stability and longer wearing life for the hiding system.

The advantage of using a dispersing agent is shown in figure 1, being noticed that when it is used the dispersion of filler materials is considerably supported enabling an increase of filler content and leading to the creation of a product easy to move from one plant to another. This difference- with and without dispersing agent- was studied for V1 variant as shown in figure 1.

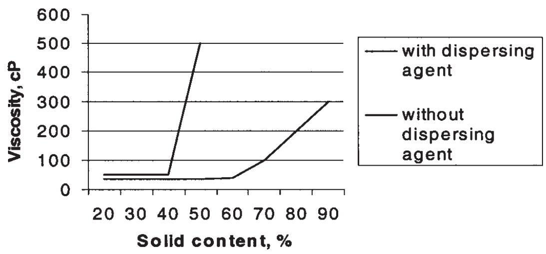


Fig. 1. Influence of the dispersing agent on the filler for V1 variant

All five variants were made using a polyphosphate dispersing agent. Thus, V4 variant was considered the most suitable in terms of characteristics obtained for replacing the polyphosphate dispersing agent with a polyacrylate dispersing agent in 1:1 ratio, thus obtaining V6 variant. The quality and influence of this replacement is determined by measuring the rubbing fineness using the grindometer. Table 5 presents the measurement values obtained after replacing the dispersing agents.

Table 5

INFLUENCE OF THE DISPERSING AGENT ON PAINT QUALITY

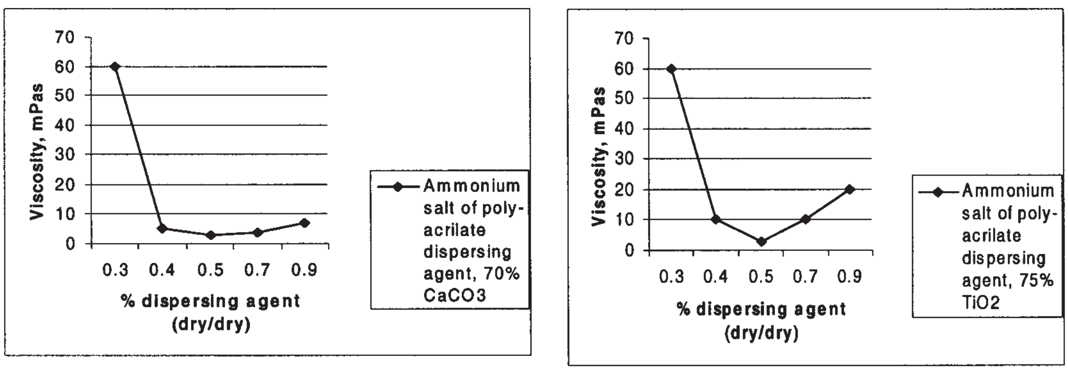
Parameters / Dispersing Agent	V 4 with poly-phosphate	V 6 with poly-acrylate
Contrast Ratio, CR, %	99.11	99.47
Fineness of the paste	40	25
Sagging resistance	12	17
Water resistance	poor	excellent

In V6 variant, the polyacrylate dispersing agent helped to the deflocculation of the fillers and pigments and contributed to the stabilization of the particles by electrostatic and steric rejection because the aggregates and agglomerations formed are considered limited and capable of ensuring a very good stability of the formulation without increasing viscosity. The influence of the polyacrylate in V6 variant was also found in the case of titanium dioxide as shown in figure 2.

Note that the polyacrylate dispersing agent also contributed to the water resistance increase of the paint film applied from the V6 variant, to the improvement of paint film hardness and to the prevention of depositing during storage as shown in table 5 and figure 5.

Tinting compatibility

Decorative architectural paints having a more or less intense color are increasingly required on the paint market.



(a) (b)

Fig. 2. (a) and (b) – Influence of dispersing agent on the filler and titanium dioxide in the V6 variant

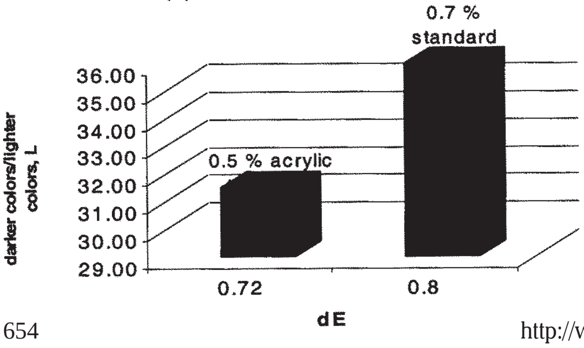


Fig. 3. Variation of color stability for V3 and V2 variants after adding 5% black pigment

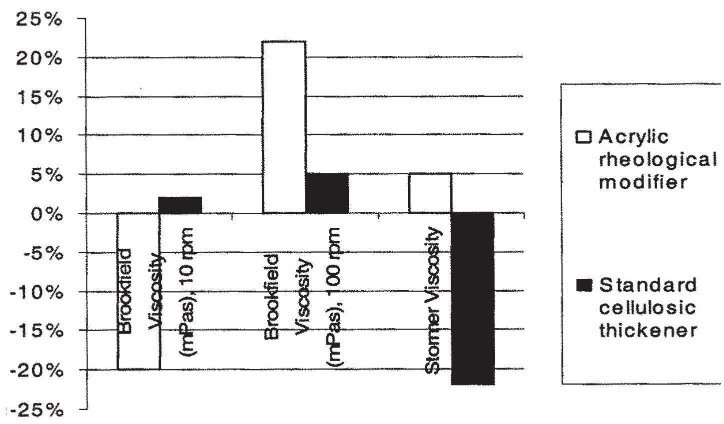


Fig. 4. Variation of Brookfield and KU viscosities for V3 and V2 variants

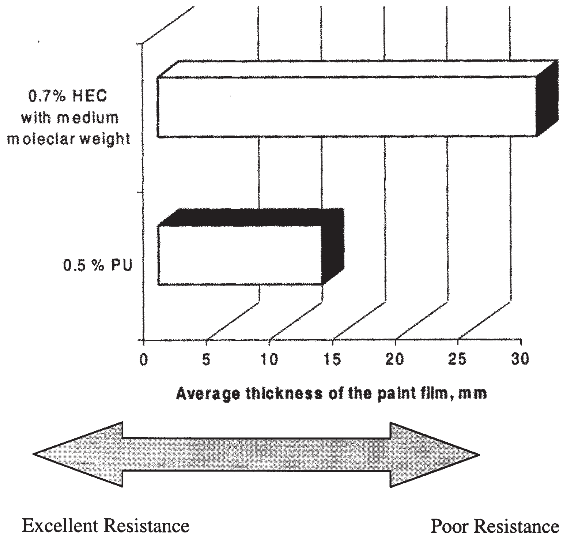


Fig. 5. Water resistance

A very good result in terms of tinting compatibility should not be overlooked. In some cases, lack of stability after adding the colorants can lead to separation of pigment easily visible to the "rub out" test. Using a universal colorant for paint tinting may lead to "drop viscosity" (drop which can lead to significantly lower viscosity) especially in intense colors.

All five variants obtained were tinted in a deep (intense) color, the same amount of color being used for all of them - 5% black pigment being noticed the effect of drop viscosity measured as a value of ICI viscosity, re-measured after staining, according to table 4. The first two variants presented a sudden ICI viscosity, thus leading to serious spattering problems, however, because in the black colorant there were high amounts of surfactant which interacts with the final groups of the associative modifiers used in V3, V4 and V5 variants, for absorbing the hydrophobic resin particles from the formulation. This interaction between the associative rheology modifiers and the resin is disturbed resulting in a weakly thickened network as indicated by the viscosity values obtained at V3 and V4 variants which presented, due to HASE and HEUR rheology modifiers used, ICI differences compared to the values before staining, but the characteristics of V5 are remain within the limits even after staining.

Comparing the color stability obtained in all five variants used there can be noticed that V3 variant presents a better stability than V1 and even V2 variant in which a bigger amount of standard cellulosic thickener was used. This is indicated in the dE value; the lower this value is the more stable the color is as shown in figure 3.

Acrylic thickener used in V3 variant presents a better stability of the color compared to the standard cellulosic thickener (V2) after adding 5% black pigment.

Viscosity variation after tinting with 5% black pigment compared between a paint containing acrylic modifier (V3) and a paint containing standard cellulosic thickener (V2) is shown in figure 4.

Using a rheology modifier also leads to obtaining a low VOC and also color stability even in the presence of a difficult colorant such as the black one that we used in the five variants studied.

Water resistance

The data acquired and presented so far indicate that rheology modifiers are excellent solutions for increasing the performance of the final product, such as film quality, water resistance, film hardness.

Water based architectural coatings must have not only protective and decorative properties but also properties related to the appearance and smoothness of the film obtained after the paint applied dries. Fine-touch coatings are obtained by using polyurethane rheology modifiers (V4 and V5) which finally render a film with a low VOC and solvent-free as presented in table 4.

Exterior paints must be resistant to heavy weather conditions such as rain, frost, while the interior ones should have a high resistance to wet scrub test (water resistance).

The test relating to the water resistance of paints with polyurethane modifiers compared to paints with standard cellulosic thickener is shown in figure 5.

A critical disadvantage of the standard cellulosic thickener and also of the most acrylic thickeners, compared to polyurethane thickeners is related to their hydrophilic nature leading to the lowest results in terms of water repelling. In other words, a polyurethane rheology modifier makes the paint film repel water than the cellulosic thickener does.

The properties of rheology modifiers enable their use in other water-based decorative systems. Interior and exterior walls are painted in order to hide the visible defects providing a nice and uniform appearance to ensure the necessary level of protection against different aggression substrates: dirt, smoke, moisture [9-10].

Besides their basic functions water based coatings are also used for decorative purposes and therefore should also offer optical properties (gloss, frost) and develop the best colors. These targets can be achieved by using HEUR or HASE rheology modifiers carefully selected according to the recommendations of the producer.

This study indicates that the performance of a paint are in close correlation with the use of rheology modifier either HEUR or HASE, or combinations thereof, depending on the expected performances.

Rheology modifiers analyzed (HASE, HEUR) are also recommended for other uses such as other decorative items like wood lacquer or textured coatings applied to interior or exterior in order to hide imperfections in the wall, contributing to stability in storage, ease of application and work for texture paint.

Reducing the levels of volatile organic compounds (VOC) is another critical target which is reached using HEUR or HASE rheology modifiers, encouraging paint manufacturers to find alternatives to solvent-based coatings, to replace them by water-based paints and to re-formulate the existing water-based paints [15-18].

One of the problems arising from the passage from a solvent system to a water-based system is the loss of rheological balance, which explains the need to use additives able to increase consistency and to ensure a flexible rheology control system. Rheology modifiers offer perfect solutions for improving the performance of formulations being at the same time environmentally friendly and complying with environmental protection laws [19-20].

Conclusions

This study offers the following conclusions:

- dispersing agents and rheology modifiers are essential points in the formulation of a decorative paint; they should be chosen so as to achieve the parameters set from the early launch;

- in an acrylic latex emulsion, using a medium molecular weight cellulosic polymer, it is very important to use a dispersion agent required for the fillers and for the pigments used. By using a polyacrylic dispersion agent, the paint will ensure a better dispersion of the fillers, a better hiding power and a better paint stability due to the lack of sedimentation;

- the remaining performances of the paint are provided by the use of rheology modifiers; thus, a HEUR rheology modifier will provide an excellent flow and leveling of the paint film applied and also a very good water resistance after drying; the HASE rheology modifier will provide resistance to spattering, a good color acceptance and easy application.

All the recipes, their combination and quantities used within the laboratory surveys are those recommended in the data sheets and can be adjusted by laboratory tests by each researcher in part, according to the other raw materials of the recipe such as resin, PVC, VOC, but also to the final parameters which are an important target for that final formula.

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