STABILIZATION OF NEPHELINE SYENITE FILLER IN A UV-CURE
POLYURETHANE DISPERSION WOOD COATING AND
VISCOSITY STABILIZATION OF TINTED
LATEX ARCHITECTURAL COATINGS

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TITLE: Stabilization of Nepheline Syenite Filler in a UV- Cure
Polyurethane Dispersion Wood Coating and Viscosity
Stabilization of Tinted Latex Architectural Coatings

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PART I ABSTRACT

STABILIZATION OF NEPHELINE SYENITE FILLER IN A UV-CURE POLYURETHANE DISPERSION WOOD COATING

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Nepheline syenite is a naturally occurring, silica deficient, sodium potassium aluminum silicate functional filler used in polymeric coatings, adhesives, and inks. Due to its unique optical characteristics, it can be utilized in formulating a low-viscosity polyurethane dispersion UV-cure clear wood coating system to enhance its functional properties. However, when the coating is formulated with the ultrafine filler, especially at a high loading level (e.g. >10% solids), the filler rapidly settles after formulated, forming a densely packed sediment layer shortening its shelf-life. Suspension of the filler was attempted using rheology additives while minimizing their negative effects on the coating's optical properties. Compatibility of the additives in the polyurethane dispersion system was qualitatively screened using a starting-point UV-cure polyurethane dispersion formulation. A design of experiments was set up to investigate optimum loading levels of the additives given by the screening step. The starting-point formulation was modified using the potential additives at the optimum loading levels and nepheline syenite with a median particle size of 1.7 μm (Minex 12[®]) at 15% solids. The starting-point formulation was also modified with both rheology additives. The modified samples were heat-aged for up to 28 days at 50°C to evaluate their anti-settling performance. Optical properties, pH, package stability and viscosity of the samples were also assessed.

A polymeric dispersant was used to prepare a nepheline syenite slurry, which was then incorporated into the polyurethane dispersion formulation. As previously discovered, the polymeric hyper-dispersant, Solsperse 46000 at 8%, was the best dispersant. Therefore, this dispersant was used in all the modified samples.

Soft-pack settling was observed in most samples modified with the rheology additives. The sediments could be re-dispersed into the coating system. A near-perfect suspension of the filler was observed in a 1.0% Rheotech 4800 modified sample. A pH drop in the sample lowered

the viscosity and increased the haze significantly to 6%. The best optical properties were obtained with a combination of 0.8% Byk425 and 3.0% Aquatix8421. However, the low-shear viscosity of this sample (3500 cP/ 3.5 Pa.s) is about 3 times higher than that of the Rheotech 4800 modified sample. Although most optimized samples had soft-pack settling with some degree of suspension of the filler, their high viscosities may not be desirable in most coating formulations requiring a low-viscosity system.

Keywords: Nepheline syenite, filler, polyurethane dispersion, dispersant, rheology additive.

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TABLE OF CONTENTS

LIST OF TABLES	ix
LIST OF FIGURES	x
PART I	12
1 INTRODUCTION	12
1.1 UV-Cure Coatings	12
1.2 Waterborne UV-Cure Coating	13
1.3 Polyurethane Dispersion	13
1.3.1 UV-Cure Polyurethane Dispersion Coatings	15
1.4 Mineral Fillers in Coatings	16
1.4.1 Nepheline Syenite	16
1.5 Pigment/ Filler Dispersion in Aqueous Media	18
1.5.1 Wetting and Separation	18
1.5.2 Stabilization	18
1.5.3 Electrostatic Repulsion	19
1.5.4 Steric Repulsion	21
1.5.5 Electrosteric Repulsion	22
2 MATERIALS AND METHODS	23
2.1 Preparation of Slurry and PUD Starting-Point Formulation	23
2.2 Application of Coating Film Samples	24
2.3 Measurement of Optical Properties	24
2.4 Rheology Profile Measurement	25
2.5 pH Measurement	25
2.6 Assessment of Accelerated Package Stability	25
3 RESULTS AND DISCUSSION	26
3.1 Step1. Additives Screening	27
3.1.1 Qualitative Screening of Dispersants	27
3.1.2 Qualitative Screening of Suspending Aids	28
3.1.3 Qualitative Screening of Rheology Modifiers with 8% Solsperse 46000	29
3.2 Step 2. Design of Experiments	30
3.2.1 Study of Interactions between Rheology Modifiers and Suspending Aids	30
3.2.2 Investigating Optimum Loading levels of Solsperse 46000 and Acrysol RM 825 ...	33
3.2.3 Investigating Optimum Loading Level of Selective Additives	34
3.3 Step 3. Modification of PUDs with Selective Rheology Additives	38
4 CONCLUSIONS AND RECOMMENDATIONS	44
PART I: REFERENCES	45
5 APPENDIX A	46
6 APPENDIX B	48
7 APPENDIX C	49
PART II	56

8	INTRODUCTION	56
8.1	Acrylic emulsion latex	56
8.2	Emulsion Polymerization	57
8.3	Rheology	57
8.3.1	Viscosity Profiles.....	59
8.4	Thickeners	60
8.5	HEC Thickeners	61
8.6	HEUR Thickeners.....	63
8.7	Effect of Colorant Addition	64
9	EXPERIMENTAL MATERIALS AND METHODS	65
9.1	Pastel Paint Formulation	65
9.2	Tinting	66
9.3	Rheology Characterization	67
9.3.1	Krebs Units (KU) Viscosity Measurement.....	67
9.3.2	Rheology Characterization with Rheometer.....	67
10	RESULTS AND DISCUSSION.....	68
10.1	Percent Solids by Weight and Stormer Viscosity of Pastel Bases	68
10.2	Viscosity Profile of Pastel Bases	68
10.3	Effect of Addition of Colorants on Viscosity of Pastel Bases	69
10.4	Effect of Type of Thickener on Tinting Strength	76
11	CONCLUSION AND RECOMMENDATIONS.....	78
	PART II: REFERENCES	79

LIST OF TABLES

Table 1. Advantages and Limitations of UV Cure Coatings	13
Table 2. A Starting-Point PUD Formulation with 15% Solids NS (Minex 12).....	23
Table 3. Minex 12 Slurry	24
Table 4. Settling Characteristic of Dispersant Candidates.....	28
Table 5. Performance of Suspending Aids in PUD Systems.	29
Table 6. Qualitative Results of Performance of Rheology Modifiers in PUD Systems	30
Table 7. Loading Levels Rheology Modifiers And Suspending Aids	31
Table 8. Loading Levels of Acrysol RM825 and.....	33
Table 9. Loading levels for dispersant, rheology modifier,	35
Table 10. Modification of PUD with Selective Rheology	39
Table 11. Formula of 1.0% Rheotech 4800 Optimized PUD Formula.....	44
Table 12. Dispersant Candidate	46
Table 13. Suspending Aid Candidates	46
Table 14. Rheology Modifier Candidates	46
Table 15. Results of Interactions between Aquatix8421 with Suspending Aids	49
Table 16. Results of Interactions between Acrysol RM825 with Suspending Aids	50
Table 17. Results of Interactions between Acrysol RM825 and RM2020, and Suspending aids..	51
Table 18. Results of Study of Effect of Solsperse 46000 Concentration.....	52
Table 19. Study of Interactions of a Dispersant, Rheology Modifier, and Suspending Aid.....	53
Table 20. Results of PUD Samples Optimized with Rheology Additives.....	54
Table 21. ICI Builders and KU Builder used for Formulations	65
Table 22. Pastel Base Paint Formulations with Different KU Builders.....	66
Table 23. Colorants used for Tinting	67
Table 24. Percent Solids by Weight and KU Viscosity of Pastel Bases	68

LIST OF FIGURES

Figure 1. Preparation of PUD using Acetone Process	14
Figure 2. Film Formation Process of a PUD Coating System	16
Figure 3. Particle Shape of NS under SEM at 5000x.....	17
Figure 4. Stabilization of Particles by Steric and Electrostatic Repulsion.....	19
Figure 5. DLVO Theory	21
Figure 6: Test Conditions for Study of Interactions between Suspending Rheology Additive	31
Figure 7: Test Conditions for Study of Effect of Solspense 46000's Concentration.....	33
Figure 8: Optical properties Acrysol RM825 and Solspense 46000 Modified Sample.....	34
Figure 9: Test conditions for Study of Interactions between Rheology Additives	35
Figure 10: Effect of Solspense 46000 Concentration on Optical Properties	36
Figure 11: Optical Properties of Aquatix 8421 and Byk 425 Modified Sample.....	37
Figure 12: Optical Clarity of Optimized PUD Samples	39
Figure 13: Gloss at 60° of Optimized PUD Samples.....	40
Figure 14: Haze of Optimized PUD Samples	40
Figure 15. Brookfield Viscosity of Optimized PUD Samples	41
Figure 16. pHs of Optimized PUD Samples.....	42
Figure 17: Separation Layers of Optimized PUD Samples After Heat-aged.....	43
Figure 18. Shear Deformation due to an Applied Force	58
Figure 19. Time Dependent Viscosity Profiles	59
Figure 20. Viscosity Profiles of Thixotropic System.....	60
Figure 21. Viscosity Profiles of Cellulosic and Associative Thickeners	61
Figure 22. HEC Type Thickener.....	61
Figure 23. Thickening Mechanism of HEC Thickeners	62
Figure 24. HEUR Type Associative Thickener	63
Figure 25. Thickening Mechanism of HEUR (Associative Thickeners)	63
Figure 26. Mechanism of Viscosity Loss upon Tinting/ Addition of Colorants.....	64
Figure 27. Viscosity Profiles Untinted Pastel Bases Thickened With Five Different Thickeners.....	69
Figure 28. Viscosity Profiles Of Tinted HEC Thicken Pastel Bases.....	70
Figure 29. Viscosity Profiles Tinted Acrysol RM995 Thickened Pastel Bases.....	72
Figure 30. Viscosity Profiles Tinted Acrysol SCT 275 Thickened Pastel Bases.....	73

Figure 31. Viscosity Profiles Tinted Optiflo-TVS Thickened Pastel Bases	74
Figure 32. Viscosity Profiles Tinted PU 1191 Thickened Pastel Bases	74
Figure 33. Viscosity Dependence Of Surfactant Concentration	75
Figure 35. Tint Strength of Tinted Pastel Bases Thickened with Five Different Thickeners	76

PART I

i INTRODUCTION

1.1 UV-Cure Coatings

A curing technique that allows instant crosslinking of monomers and oligomers is the radiation curing technique (Koleske 1986). The crosslinking due to a radiation energy leads to a transformation of coating liquids into the solids instantaneously (Koleske 1986). The radiation curing process can be either ultraviolet (UV) radiation for UV cure coatings or electron beam (EB) radiation for EB cure coatings. Only UV-cure coating with free radical polymerization is discussed in this paper. UV-cure coatings are generally composed of monofunctional or multifunctional monomers, oligomers, additives and a photoinitiator package. Curing of UV-cure coatings normally involves either free radical or cationic initiated addition polymerization reactions. The free radical polymerization reaction can be used for both linear polymerization of monofunctional monomers and crosslinking polymerization of multifunctional monomers; both polymerizations involve same reaction steps: radiation initiation, propagation, chain transfer and termination, but the chain transfer and the termination of these two polymerization reactions can have different mechanisms (Andrzejewska 2001). Acrylate monomers are widely used in UV-cure coating and undergo the free radical polymerization reaction (Andrzejewska 2001).

UV-cure coating technology has been used for numerous applications in industry. These industries include, but are not limited to, printing, automotive, furniture, communication, electronics, and health care. However, this curing technique has both advantages and limitations in applications as described below in Table 1.

Table 1. Advantages and Limitations of UV Cure Coatings

Advantages	Limitations
Lower Energy Consumption	Curing irregular shapes
Heat sensitive substrates	Pigmentation: leveling
Instantaneous cure	Pigmentation: curing
100% solids	Photo-degradation
No VOCs	Shrinkage
Safety	Curling

(Z. Wicks et al. 2007)

1.2 Waterborne UV-Cure Coating

The invention of latex architectural coatings was the first step toward replacing solventborne coatings with waterborne coating systems. The US government's environmental regulations in 1970s and 1980s further motivated the coating industries to replace solventborne systems. Dispersion in water technology led the development of waterborne UV-cure coatings. The dispersion technology eliminates the use of reactive diluents in coatings so that emission of VOCs can be almost zero. Since the coating's viscosity is independent of molecular weight, it can be thinned with water. Adhesion of waterborne UV-cure coatings is superior to that of conventional UV-cure coatings due to reduced shrinkage during curing. Improved exterior durability can be obtained with the waterborne coatings by blending with other waterborne coatings (Z. Wicks et al. 2007).

Curing of a waterborne UV-cure coating involves one additional step, force drying. This additional step is considered as a drawback in the curing process of the coatings. Force drying is carried out in an oven at 80°C before the UV curing, however, the temperature can be varied. Furthermore, in some cases, the waterborne coatings also require flash-off the water at ambient temperature for several minutes (e.g., 10 minutes) prior to the force drying.

1.3 Polyurethane Dispersion

Polyurethane dispersion (PUD) coatings have been available on the market since the 1970s (Kim 1996). PUDs are sometimes referred to polyurethane latexes since PU solids are dispersed in water (Z. Wicks et al. 2007). PUDs are prepared with dispersion polymerization,

whereas latex emulsion coatings are formulated by emulsion polymerization (Asua 1997). PUDs are one-component systems and are environmentally friendly due to their low to zero VOCs. High molecular weights can be achieved at low viscosity (Kim 1996).

PUDs are prepared using three different processes, namely, acetone process, prepolymer mixing process, and melt dispersion process. As an example, the acetone process is shown below in Figure 1.

Figure 1. Preparation of PUD using Acetone Process (Kim 1996)

PUDs are generally made with diisocyanates, polyols, and chain extender amines. Aliphatic isocyanates (NCO) such as 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI), isophorone diisocyanate (IPDI), and 1,6-hexamethylene-diisocyanate (HDI) are favorable to use in PUD preparations due to the low reactivity of their NCO groups in water (Kim 1996). Different types of polyols can be used to tailor the polyurethane backbones. Polyesters,

polyethers, and polycarbonates are considered as soft segment polyols whereas diols and triols are used as hard segments. Chain extender tri- or diamines react with the isocyanates faster than with water leading to chain extension of NCO-terminated prepolymers. This chain extension increases molecular weight as well as modulus, strength, thermal stability, and water and solvent resistance. Anionic, cationic, and nonionic dispersants can be used (Kim 1996).

1.3.1 UV-Cure Polyurethane Dispersion Coatings

Without both the dispersion and radiation cure technologies, it would not be possible to make UV-cure PUD systems. UV-cure PUDs are colloidal dispersion systems with low to zero VOCs. They are stabilized with electrostatic repulsion between the colloids (Tielemans et al. 2006). UV-cure PUD systems are prepared by crosslinking PU with acrylates. The lower crosslinking density and the higher average molecular weight between crosslink points provide excellent chemical resistance and mechanical properties (Tielemans et al. 2006). Furthermore, solvent and chemical resistance is increased by double bond conversion of acrylates when the coatings are cured with UV radiation. The superior properties of UV-cure PUDs provide the exterior durability needed for protection of wooden materials that are anisotropic and sensitive to weather, and have nonhomogeneous structures (Goldschmidt and Streitberger 2003). The excellent adhesion property resulting from low viscosity and polarity of the coating systems further offers the mechanical interlocking inside the porous substrates (Kim 1996).

Film formation and curing processes of UV-cure PUD coatings do not resemble those of acrylic latex coatings. In the UV-cure coating systems, hydrogen bonding of urethanes with water molecules plasticizes the colloidal polymer particles making film formation of PUDs possible at a low minimum film formation temperature without a coalescing aid (Tielemans and Bleus 2006). However, film formation aids are available for air-dry PUD systems to obtain high crosslink density. The formation and curing process of the PUD coatings is illustrated in Figure 2.

Figure 2. Film Formation Process of a PUD Coating System

1.4 Mineral Fillers in Coatings

A misconception for some coating formulators and end users is that mineral fillers are low-cost substitutes used solely to replace some of coating's more expensive ingredients such as resins and pigments. The purpose of addition of fillers in paints and coatings is not only to save cost but also to engineer optical properties (gloss, hiding power, etc.), to enhance physical and chemical properties (tensile strength, barrier properties, abrasion resistance, hardness, etc.), and to raise solids content. Critical properties of fillers having effects on coating properties include particle shape and size, oil absorption, brightness, Mohs hardness, reflective index, pH and specific gravity,. Common mineral fillers include silica, diatomaceous earth, calcium carbonate, synthetic silica, kaolin clay, nepheline syenite, talc, and mica.

1.4.1 Nepheline Syenite

Nepheline syenite (NS), commercially known as Minex® from Unimin Corporation, is a naturally occurring silica deficient sodium potassium aluminum silicate functional filler used in polymer filled coatings, adhesives, and inks (Remortel and Ratcliff 2010). It has a chemical composition of $(\text{Na}, \text{K}) \text{AlSiO}_4$, and its typical properties are shown in Table 2.

Table 2. Typical Properties of Nepheline Syenite

Particular Shape	Nodular/ irregular, rectangular, angular ¹
Specific Gravity (g/ml)	2.56-2.61
Mohr Hardness (1.0-10.0)	6.0
pH	9.5-10.5
Reflective Index	1.51-1.53
Brightness	85-94

¹ See Figure 3. (Remortel and Ratcliff 2010)

Figure 3. Particle Shape of NS under SEM at 5000x
(Remortel and Ratcliff 2010)

NS offers excellent brightness, tint retention, and weather durability in exterior paints. In interior paints, NS improved color, sheen uniformity, chemical and stain resistance, and durability (Remortel and Ratcliff 2010). NS is formed in a few certain geological locations, and can be produced into high purity translucent pigments suitable for radiation cure systems including coatings, adhesives, and overprint ink varnishes (Remortel and Ratcliff 2010). Newly engineered ultrafine NSs (<2.0 μ m) provide superior performance in clear wood and industrial coatings. Due to their purity of color, unique light transmission, and low reflective index characteristic, NS materials are very beneficial when formulated in powder and UV cure coating systems. Unlike most fillers and pigments, NS does not absorb the radiation energy needed to activate photoinitiators of the UV- cure systems. Thus, the energy is delivered to the systems to carry out free radical or cationic initiated addition polymerization reactions.

The cost of NSs varies according to their particle size. As of 2012-2013, NSs are commercially available in median particle sizes (d50s) of from 1.7 to 14.3 μ m. The smaller the particle size, the more it will cost. NS with d50 of 1.7 μ m costs approximately \$0.60 per pound.

1.5 Pigment/ Filler Dispersion in Aqueous Media

Dispersion of pigments in aqueous media involves three processes: wetting, separation, and stabilization. The dispersion in waterborne systems is similar to that of solventborne systems. However, the high surface tension of water makes dispersion of pigments and fillers in water-based coatings more complex.

1.5.1 Wetting and Separation

Displacement of air from a pigment surface by a liquid medium (e.g. resin solution or coating vehicle) is called wetting (Z. Wicks et al. 2007). Wetting with a low surface tension liquid is necessary to obtain a proper dispersion of pigments with low surface energy. For wetting to occur, the liquid needs to penetrate the cavities of pigment clusters and agglomerates (Goldschmidt and Streitberger 2003). The penetration rate depends on the radius of the cavities as well as viscosity of the liquid (Goldschmidt and Streitberger 2003). Either smaller cavities or higher viscosity or both will cause a slower penetration rate (Goldschmidt and Streitberger 2003). Separation processes separate pigment agglomerates into individual particles without grinding the particles into smaller particle sizes (Z. Wicks et al. 2007). This process is carried out with a dispersion machine that generates shear force and permits suspension of the particle in the liquid. Surface modification/treatment of pigments also assists efficient separation.

1.5.2 Stabilization

After the wetting and separation processes, it is crucial to maintain the suspension and separation of the pigments in the dispersion phase by stabilization mechanisms. A failure to stabilize the dispersion system leads to the pigment flocculation. In some cases, destabilization of the system results in sedimentation of the pigment, which is one of the major challenges for coating formulators. The flocculated pigment can be re-dispersed into the system under a low shear force. However, the shear may not help re-dispersing of sediments if they are densely packed. As a result, a total loss of the whole coating system will result.

Stabilization is generally accomplished by electrostatic repulsion and steric (entropic) repulsion, as shown in Figure 4. Electrostatic repulsion is a primary stabilizing mechanism for aqueous media, whereas steric repulsion is the primary mechanism for non-aqueous media.

Figure 4. Stabilization of Particles by Steric and Electrostatic Repulsion

1.5.3 Electrostatic Repulsion

The electrostatic stabilization mechanism provides particle separation by repulsion of like charges. Negatively charged particles will attract surrounding positively charged ions in their liquid medium. As two such positively-charged particles approach each other, their positive charges caused them to repel and stabilizes the particles. The repulsion force is inversely proportional to the distance between the two particles and depends on electric double layer whose thickness is given by the Debye length λ_D .

$$\lambda_D = \sqrt{\frac{\epsilon \epsilon_0 k_B T}{2 c_e e^2}}$$

ϵ = Dielectric permittivity

ϵ_0 = Vacuum permittivity

k_B = Boltzmann constant

T = Temperature

c_e = Electron concentration

e = Elementary charge. (Butt, Graf, and Kappl 2003)

The thickness of the layer depends on the ionic strength of the liquid. The thickness reduces with an increase in the ionic strength. Therefore, electrostatic repulsion is reduced, and the particles can get closer to each other due to Brownian motion resulting in aggregation.

The attractive (van der Waals) and repulsive forces acting on the dispersed particles can be determined by the DLVO (Derjaguin, Landau, Verwey, and Overbeek) theory (Butt et al. 2003)(Goldschmidt and Streitberger 2003). Attraction and repulsion potential between two identical spheres of equal radius are given by the equation V_{att} and V_{rep} , respectively, shown below.

$$V_{att} = \frac{-A R}{12 h}$$

V_{att} = Attractive potential

A = Hamaker constant (strength of attraction)

R = Particle radius

h = Particle separation

$$V_{rep} = 2\pi\epsilon\epsilon_0 R\zeta^2 \ln(1 + e^{-\kappa h})$$

V_{rep} = Repulsion potential

ϵ = Dielectric permittivity

ϵ_0 = Vacuum permittivity

R = Particle radius

κ = Inverse of Debye length (m^{-1})

h = Particle separation

These forces are also referred to as DLVO forces (Butt et al. 2003). The net (total potential) energy, V_T , is used to determine the stability of dispersion systems. The energy acting on the particles is a function of the distance between the two particles and can be calculated by adding the repulsion and attractive forces.

$$V_T = V_{att} + V_{rep}$$

At low ionic strength of the liquid, the net force indicates a very weak attraction at large distances (secondary energy minimum), an electrostatic repulsion (electrostatic barrier) at intermediate distance, and a strong attraction at short distances (primary energy minimum), as shown in Figure 5. At high ionic strength, the repulsion barrier that prevents from aggregation diminishes; as a result the attractive force dominates at any distance.

Figure 5. DLVO Theory
(Goldschmidt and Streitberger 2003)

To attain the stability of the particles, the aqueous coatings should not be formulated near a pH equal to the isoelectric point (IEP) where zeta potential is zero. Around the IEP, the colloidal system is least stable indicating that repulsion forces are weak to keep the particles separated. Therefore the particles collide and flocculation will occur. In other words, the IEP is a pH that should be avoided in dispersion systems. The recommended zeta potential of the particles should be -30 mV at a high pH or +30 mV at a low pH to avoid the unstable IEP region.

1.5.4 Steric Repulsion

Steric stabilization is obtained from the repulsion forces of adsorbed polymer layers at the surface of particles when they approach each other. The repelling of polymer layers reduces conformations of the polymer molecules; therefore it reduces the entropy of the layers. According to the Gibbs-Helmholtz equation,

$$\Delta G = \Delta H - T\Delta S,$$

the free energy (G) becomes more positive as the entropy (S) decreases, which favors destabilization of particles. Steric stabilization is improved by increasing the absorbed polymer

layer thickness. The thickness can be increased using adsorbed polymer layers having conformations of block, brush or comb copolymer chains.

1.5.5 Electrosteric Repulsion

The combination of the both steric and electrostatic stabilizations is required in some aqueous coating systems when the electrostatic stabilization alone is not sufficient. The combination is known as electrosteric or mixed stabilization. This type of stabilization is needed when aqueous coatings are formulated with hard water containing counter-ions. Many coating ingredients such as pigments and mineral fillers have ionic contaminants and ionic components from manufacturing process, which enter the water and interfere.

2 MATERIALS AND METHODS

In this study, long-term stability and optical clarity were optimized for an aqueous UV-curable polyurethane resin dispersion (PUD) system containing ultrafine NS filler. A starting-point formulation is shown in Table 2. For this optimization, five dispersants, four suspending aids, and eight rheology modifiers were evaluated. The additives used were recommended by suppliers to provide long-term dispersion and suspension of ultrafine NS, while maintaining optimum clarity and compatibility in the PUD system. These additives are listed in Appendix A, Tables 14, 15, and 16.

Table 2. A Starting-Point PUD Formulation with 15% Solids NS (Minex 12)

Item	Wt.(g)	Type
Charge under agitation		
Bayhydrol UV VP LS 2317	100	Polyurethane Dispersion
Irgacure 500	1.5	UV-cure agent
Min 5 min, then add		
Minex 12 Slurry with 8% Solsperse 46000	4.68	Resin Free Dispersion
Mix 15 min at ~2000rpm		
DI Water	27.34	DI water
BYK 346	0.62	Defoamer
Mix 10 min, approx. 800 rpm		

2.1 Preparation of Slurry and PUD Starting-Point Formulation

The above Minex 12 PUD starting-point formula was originally formulated at 12% Minex 12. This filler loading was found in previous work done by Unimin to provide the best functional performance. Unimin evaluated Minex 7, 10 and 12 grades at 0, 6, 12, and 18%; the best functional performance was observed at 12% solids with Minex 12.

In this study, the Minex 12 loading was increased to 15%, based on clear resin solids in the cured film, to simulate higher loading conditions. The standard and stable Minex 12 slurry (resin-free pre-dispersion) recipe was utilized to incorporate Minex 12 into PUD formulation, provided in Table 3.

Table 3. Minex 12 Slurry

Item	Wt. %
Tap Water	29.26
Add the following under agitation	
Solsperse 46000 (50% solids)	9.76
Mix for 5 minutes at 1000 rpm	
Minex 12	60.99
Mix for 10 minutes at 2000 rpm	
Total	100.00

The PUD systems were prepared with a CV-3E mixer from VMA-GATZMANN GMBH. The volume of the mixing container and the size of the blade depended on sample size. In general, the diameter of the blade was about one-third of the container. Samples were allowed to sit overnight at room temperature before initial assessment.

2.2 Application of Coating Film Samples

Two different drawdown methods were used, depending on the type of evaluation needed. Drawdowns on Leneta drawdown charts (Form 3B) were applied with a 6-mil Bird film applicator to prepare samples for measuring optical clarity and gloss at 60°. In addition, drawdowns were applied on 4x8" transparent glass panels using a 10-inch wire-wound rod film applicator of size 28 from BYK-Gardner to prepare samples for haze measurement. Wet coating films were successively air-flashed for 10 minutes at room temperature, force-dried in an oven at 50°C for 10 minutes, and UV-cured (LCN-06-1-T3 from American Ultraviolet Company with 200Watt/inch at a belt speed of 33FPM).

2.3 Measurement of Optical Properties

Haze and optical clarity of dry films were measured with a hazemeter (Haze-Gard Plus by BYK-Gardner). Values were averaged over three measurements at different locations of the glass panel. Gloss at 60° was measured with a glossmeter (Progloss from Hunter Associates Laboratory Inc.). Gloss measurements were made on the black portion of the Leneta drawdown charts.

2.4 Rheology Profile Measurement

Rheology profiles of coating samples were measured with a programmable Brookfield Viscometer (RVDV-II+Pro EXTRA from Brookfield Engineering Labs, Inc.), using an SC4-21 cylindrical-type spindle. The sample chamber for the spindle was 13R, which requires 7.1 ml of coating samples. The viscometer was programmed to measure viscosities at 0.5, 5, 10, 25, 50 and 100 RPMs. Data were collected at each RMP for 2 minutes.

2.5 pH Measurement

pH values of coating samples were measured using a pH meter (Accument pH meter 25 from Fisher Scientific).

2.6 Assessment of Accelerated Package Stability

Accelerated package stability was tested in an oven at 50°C for 1, 2, and 4 weeks, depending on type of evaluation. Prior to the test, samples were allowed to sit overnight, stirred to re-disperse any amount of settling, and transferred to 4-oz glass test jars. These jars were filled with 80 mL of coating sample. Samples were cooled down to room temperature before any testing.

Assessment of the heat-aged samples involved measurement of syneresis layers of the coating samples, if there was any. The sediment height was also measured. Settling ratings were determined according to ASTM D869-85 and are listed in Appendix A. A spatula of 15 ± 1 g with 8 mm (0.315 inch) wide tip and 203 mm (8 inch) length was used to stir the samples up to 300 times in clockwise and counter-clockwise directions. In some cases, some samples could not be remixed homogeneously due to excessive flocculation or agglomeration. Additional assessment of aged samples involved measurement of pH, rheology profiles, optical clarity, haze, and gloss at 60° as described above.

3 RESULTS AND DISCUSSION

Until recently, clear wood and industrial coating formulators did not have a high-clarity mineral filler that was capable of being loaded at high levels (i.e., approaching 20% by weight) while providing good optical clarity and gloss. Ultrafine nepheline syenite fillers such as Minex 12 and even finer future versions (e.g. Minex 14, Minex 16) have been formulated in clear resin systems at loading levels approaching 20 % while maintaining excellent optical clarity. The challenge for formulators of these low solids and low-viscosity aqueous systems is to achieve adequate long-term dispersion and suspension of these high-density ultrafine NS fillers without compromising the optical quality. This is in contrast to high-solids, high-viscosity decorative paints, which are modified with rheological and suspending additives and in which all NS fillers are readily suspended. In low-viscosity and unmodified aqueous systems, settling of high-density micron-size NS fillers occurs within a short period of time after dispersion and shortens in-can stability and shelf life. If filler is allowed to settle and then hard-pack, it cannot easily be re-incorporated into the coating system, rendering it unusable.

The approaches used in this project to improve dispersion properties of ultra-fine nepheline syenite can be understood by considering fundamental principles that govern settling of particles. The well-known equation for the theoretical steady-state sedimentation velocity derived from Stokes' Law is given by:

$$v = \frac{2}{9} \frac{R_s^2(\rho_2 - \rho_1)g}{\eta}$$

where v is the particle's settling velocity, R_s is the radius of the spherical particle, ρ_1 and ρ_2 are densities of the liquid and the particle, respectively, η is the dynamic viscosity, and g is the gravitational acceleration. Rheology modifiers were used to increase the viscosity and thereby slow down settling. Alternatively, precipitation can be retarded by decreasing the particle size. Note that the correlation between settling velocity and particle size is quadratic. Specifically, next-generation submicron-sized Minex grades are expected to have significantly improved settling properties compared with Minex 12.

Polymeric hyper-dispersant Solsperse 46000 was proven to make a stable slurry with Minex 12 (Remortel 2010). However, hyper-dispersant by itself cannot provide long-term package stability in PUD formulations. In addition to using this type of dispersant, suspending aids and low-shear rheology modifiers were considered to develop a better suspension with minimum negative impact on application performances, most importantly optical properties of the system. A systematic approach was used to screen and identify additive candidates that were compatible with the PUD system.

3.1 Step 1. Additives Screening

3.1.1 Qualitative Screening of Dispersants

In the initial stage of this project, the starting-point slurry formula was used to screen five other new and promising dispersants shown in Table 4. The dispersant loadings were based on Minex12 solids. The candidates showed package stability from semi-hard to hard packing, which can be seen in the table. The formulation with 8% Solsperse 46000 provided by far the best anti-settling characteristic. Further optimization of the starting PUD formulation was conducted with this dispersant. In previous work by Unimin (Remortel 2010), 8% Solsperse 46000 also gave the best dispersion and package stability and the least settling when compared to other candidates.

Table 4. Settling Characteristic of Dispersant Candidates

Dispersants	Settling Characteristic (1)
8% Solsperse 46000 (Standard)	Soft to No Pack
1% and 5% Zephrym PD 3300B	Hard Pack
1% and 5% Zephrym PD 4974	Hard Pack
6% Solsperse 46000 + 2% Disperbyk 2010	Hard Pack
6% Solsperse 46000 + 2% Disperbyk 2015	Semi-Hard Pack
4% Solsperse 46000 + 4% Disperbyk 2010	Semi-Hard Pack
4% Solsperse 46000 + 4% Disperbyk 2015	Semi-Hard Pack
4% and 8% Disperbyk 2010	Hard Pack
4% and 8% Disperbyk 2015	Hard Pack

(1) Soft pack: Sediments are loosely packed and can be re-incorporated into coatings;
Hard pack: Sediments are tightly packed and cannot be re-incorporated into coatings;
Semi-pack: Sediments are slightly hard pack but can be re-incorporated into coatings

3.1.2 Qualitative Screening of Suspending Aids

After the dispersant screening, a total of four suspending aids, Table 5, were screened in a formulation with 15% Minex 12 to investigate which candidates could give film clarity, high gloss, package stability and ease of re-dispersion. These additives were used at manufacturers' recommended loading levels. The collected qualitative positive or negative results (+/-) were relative to those of the PUD standard sample with no suspending aid. Anti-Terra 250, Laponite EP and Byk 425 showed soft packing and ease of re-dispersion with the least impact on gloss while maintaining the dry film clarity. These suspending aids were selected for future studies.

Table 5. Performance of Suspending Aids in PUD Systems.

Suspending Aids (1)	Film Clarity (2)	Gloss 60°	Settling Characteristic	Ease of Re-dispersion
None (Standard)	Clear	~94	Hard Packing	No
0.2% Laponite EP	-	-	-	=
0.5% Laponite EP	-	-	-	=
0.25% Laponite EP*	=	-	+	+
0.5% Laponite EP*	-	-	+	+
0.2% Laponite RD	=	-	-	=
0.5% Laponite RD	=	-	-	=
0.25% Laponite RD*	-	-	+	+
0.5% Laponite RD*	-	-	+	+
0.5% Anti-Terra 250	=	-	+	+
2.5% Anti-Terra 250	=	-	+	+
0.5% BKY 425	=	-	+	+
2.5% BKY 425	=	-	+	+

(1) * added as 5% solution in water

(2) + : Superior compared to the standard sample;

- : Inferior compared to the standard sample;

= : Equal performance compared to the standard sample

Loadings are based on total formulation weight.

3.1.3 Qualitative Screening of Rheology Modifiers with 8% Solsperse 46000

Seven rheology modifiers were screened at minimum and maximum loading levels. As shown in Table 6, only formulations with Aquatix 8421, Acrysol RM825, Acrysol RM2020, Rheotech 4800, and Dsx 3291 showed good film clarity and improved package stability and ease of re-dispersion while minimizing impact on gloss. These rheology modifiers were used in the successive DOE study to optimize the dispersant, suspending aid and rheology modifier package.

Table 6. Qualitative Results of Performance of Rheology Modifiers in PUD Systems

Rheology Modifiers (1)	Film Clarity (2)	Gloss 60°	Settling Characteristic	Ease of Re-dispersion
None (Standard)	Clear	~94	Hard Packing	No
2.0% Aquatix 8421	=	-	+	+
2.0% Acrysol RM825	=	-	+	+
2.0% Acrysol RM2020	=	-	+	+
2.0% Acrysol RM825/ Acrysol RM2020 (50% :50%)	=	-	+	+
2.0% Optigel WX	-	-	+	=
2.0% Optigel WX*	-	-	=	+
2.0% Disparlon AQH-800	-	-	+	+
1.0% Rheotech4800	=	-	+	+
1.0% Dsx 9231	=	-	+	+
1.0% Polyphobe HE106	-	-	=	-

(1) * added as 5% solution in water

(2) + : Superior compared to the standard sample;

- : Inferior compared to the standard sample;

= : Equal performance compared to the standard sample

Loadings are based on total formulation weight.

3.2 Step 2. Design of Experiments

3.2.1 Study of Interactions between Rheology Modifiers and Suspending Aids

A central composite design of experiment (DOE) for two factors (2^2) was set up to study the effects of rheology modifier and suspension aid on suspension and optical properties of the starting-point formula, Figure 6. The rheology modifiers and suspending aids are listed in Table 7. This design generated five test conditions for each combination of the three rheology modifiers and three suspending aids (5 test conditions= 2^2 corner test conditions and 1 face center test condition). Samples were heat-aged for 7 days at 50°C. The DOE experiment results are provided in Appendix C, Tables 15, 16, and 17.

Figure 6: Test Conditions for Study of Interactions between Suspensing Rheology Additive

Table 7. Loading Levels Rheology Modifiers And Suspensing Aids

Rheology Modifiers	Loading (%)
Aquatix 8421	1.0, 3.0, and 5.0
Acrysol RM825	1.0, 3.0, and 5.0
Acrysol RM825/Acrysol RM2020 (50/50)	1.0, 3.0, and 5.0
Suspensing Aids	
Anti Terra 250	0.0, 1.25, and 2.5
Byk 425	0.5, 2.0, and 3.0
Laponite EP solution (2.5% in water)	0.0, 1.5, and 3.0

It was found that samples prepared with rheology modifier Aquatix 8421 and suspending aid Byk 425 showed high gloss, soft packing, settling rating of 9 or 10, no syneresis (except for the -1, -1 sample), and ease of re-dispersion.

In the combination of Acrysol RM825 rheology modifier and the suspending aids, the sample formulated at 1% Acrysol RM825 and 0% Laponite EP (-1, -1 point on composite design) gave soft packing, increase in gloss at 60°, settling rating of 8, and ease of re-dispersion. This observation suggested that Acrysol RM825 performs better by itself.

The results obtained from a blend of Acrysol RM825 and Acrysol RM2020 rheology modifiers with the suspending aids were not taken into consideration since the blend is suitable only when a higher shear viscosity is desired. Some of the systems at maximum rheology modifier and suspending aid were too high in viscosity and gelled, and were not pourable. The criterion used for this screening was that the formulation would remain pourable when the bottles were turned upside down, which eliminated the Acrysol blend.

A combination of Aquatix 8421 with Byk 425 and Acrysol RM 825 by itself was chosen for further optimization of the PUD system. Rheology modifiers Rheotech 4800 and DSX 3291 were added to the DOE study as well. These candidates were identified as potentially good candidates after the first DOE study was completed.

3.2.2 Investigating Optimum Loading levels of Solsperse 46000 and Acrysol RM 825

A central composite design of experiments for two factors (2^2) was used to study the interaction of rheology modifier with dispersant, Figure 7 and Table 8. This design generated a total of ten test conditions (10 test conditions= 2^2 corner test conditions + 2 central test conditions, and 4 face center test conditions). Samples were heat-aged for 14 days at 50°C.

Figure 7: Test Conditions for Study of Effect of Solsperse 46000's Concentration

Table 8. Loading Levels of Acrysol RM825 and Solsperse 46000, Minex 12 loading 15%

Rheology Modifier	Loading (%)
Acrysol RM825	1.0, 2.5, and 4.0
Dispersant	
Solsperse 46000	6.0, 8.0, and 10.0

This study showed that the heat-aged samples decreased in haze significantly, and slightly increased in optical clarity and gloss. DOE test results are found in Appendix C, Table 18. The key surface response plots are provided in Figures 8 a, b and c. Figure 8a shows that the haze was lowest at 8.0% Solsperse 46000 and 1.0% Acrysol RM825. However, since the R^2 -value of the haze's response plot is very low ($R^2=38.5\%$), it is not appropriate to use it for haze predictions. Surface response plots of optical clarity and gloss at 60° indicated that the clarity and gloss at 60° did not depend significantly upon the Solsperse 46000 loading. While Acrysol

RM825 did not have a major effect on the gloss, however, a trend of decreasing clarity was observed when Acrysol RM825 loading was decreased.

Figure 8: Optical properties Acrysol RM825 and Solsperse 46000 Modified Sample.

3.2.3 Investigating Optimum Loading Level of Selective Additives

Another central composite design for three factors (2^3) was performed to optimize Solsperse 46000, Byk 425, and Aquatix 8421 additive concentrations in the PUD starting-point formula, Figure 9 and Table 9. This design generated a total of 15 test conditions (15 test conditions= 2^3 corner test conditions + 1 central test conditions, and 6 face center test conditions). Samples were heat-aged for 2 weeks at 50°C before testing.

Figure 9: Test conditions for Study of Interactions between Rheology Additives

Table 9. Loading levels for dispersant, rheology modifier, and suspending aids

Rheology Modifier	Loading (%)
Aquatix 8421	1.0, 2.0, and 3.0
Suspending Aid	
Byk 425	0.1, 0.8, and 1.5
Dispersant	
Solsperse 46000	6.0, 8.0, 10

The DOE test results for Solsperse 46000 added at loading levels from 6 to 10% are shown in Figure 10. The effect of the loading level of this dispersant on the optical properties was minimal. Heat aging affect the optical properties somewhat: haze decreased and gloss and clarity increased.

Figure 10: Effect of Solsperser 46000 Concentration on Optical Properties

Since the optical properties were not influenced by the loading level of Solsperser 46000 from 6 to 10% , only the surface response plots of samples prepared at 8% Solsperser 46000 are presented in this section. The surface response plots of the samples before and after the heat-aging could not be compared, due to issues with a few flocculated samples during the heat aging, which meant that a full set of data could not be collected. The data collected for the DOE is listed in Table 19 in Appendix C.

As shown in Figures 11a and 11b, haze and optical clarity improved when Aquatix 8421 and Byk 425 were used at minimum loading levels. Haze was lowest at 0.0 to 0.5% Byk 425 and 1 to 1.4% Aquatix 8421. The best optical clarity of 97% was obtained for 0.6 to 0.7% Byk 425 and 0.0 to 0.5% Aquatix 8421. Gloss was highest when Byk and Aquatix were at their lowest concentration. Since response plots of these optical properties have good correlation numbers ($R^2 > 90\%$) , predictions can be made based on the plots. Although the response plots of heat-aged samples were not available, the data showed significant decrease in haze and an increase of a few percent in both the gloss and clarity.

a) Haze ($R^2=94.7\%$)

b) Optical Clarity ($R^2=94.3\%$)

c) Gloss 60° ($R^2=91.0\%$)

Figure 11: Optical Properties of Aquatix 8421 and Byk 425 Modified Sample

3.3 Step 3. Modification of PUDs with Selective Rheology Additives

The final optimization step included a total of eight test formulas prepared with the best potential rheology and suspending additive combinations and concentrations discovered in steps 1 and 2, Table 10. The final additive levels were selected based on the best DOE space to balance optical film properties with suspension and pigment stabilization properties. Rheotech 4800 was discovered after the initial DOE tests. Its screening showed it had optical compatibility, suspension, and rheology characteristics; therefore it was added to the final round of testing. Assessments of the samples were performed initially and after heat aging for 14 days and 28 days at 50°C.

Table 10. Modification of PUD with Selective Rheology Additives and 15% NS

Rheology Modifiers	Suspending Aids
1) 2.0% Aquatix 8421	0.8% Byk 425
2) 3.0% Aquatix 8421	0.8% Byk 425
3) 3.0% Aquatix 8421	1.5% Byk 425
4) 3.0% Acrysol RM825	-
5) 4.0% Acrysol RM825	-
6) 5.0% Acrysol RM825	-
7) 1.0% Rheotech 4800	-
8) 1.5% Rheotech 4800	-

Figure 12: Optical Clarity of Optimized PUD Samples

The sample prepared with 1.5% Rheotech 4800 occurred gellation and aggregation during the heat-aging test. Optical properties of the sample could not be evaluated. It should be noted that NS (Minex 12) filler settled to some extent in most of the optimized samples, except 1.0% Rheotech 4800 modified sample where near-perfect suspension of the filler was obtained. The settling layers found in most of the samples were softly packed and could be easily re-dispersed. Optical clarity increased slightly after heat aging in most samples, Figure 12. Gloss increased by about 5% after heat-aged, Figure 13. The haze of the samples, except for 1.0% Rheotech 4800 modified sample, decreased drastically after heat-aged, Figure 14. The best explanation for the

improvement in overall optical properties after heat-aging is that the well dissolved rheology additives at 50°C were adsorbed effectively on the filler's surfaces providing steric repulsion to minimize crowding effect of the filler. If the samples were not aged at 50°C, it is not expected to see improvement in the optics.

Figure 13: Gloss at 60° of Optimized PUD Samples

Figure 14: Haze of Optimized PUD Samples

Except the 1.0% Rheotech modified sample, it was not surprising to see that there was no viscosity change in all the optimized samples during the heat-age (Figure 15), even though there was slight decrease in pH overtime (Figure 16). BYK 425 and Acrysol RM825 are associative thickeners that are not sensitive to the pH to alter the viscosity of the coatings. On the other hand, Rheotech additive is an alkali-swellable copolymer (vinyl acetate ethylene copolymer) thickener with high sensitivity to change in pH. Therefore, the viscosity of the Rheotech modified sample depended on its pH, which decreased during the heat-age. As pH drops, the copolymer coils up and reduces its hydrodynamic volume taken in the continuous media to lower the coating's viscosity. The pH drop is another cause of high percent haze in the 1.0% Rheotech sample after the heat-aged. In this particular sample, when it became more acidic both steric and electrostatic repulsions diminished due to reduction in the hydrodynamic volume of the copolymers and increasing in the ionic strength of the sample, respectively. Consequently, crowding of the filler was likely to occur to increase the haze. The complete data set of final optimization of PUD with rheology modifiers can be seen in Appendix C, Table 20.

Figure 15. Brookfield Viscosity of Optimized PUD Samples

Figure 16. pHs of Optimized PUD Samples

A chart representing the layers of separation and settling of the final test samples after 28 days of heat aging is provided in (Figure 17). Samples prepared with 1.0% and 1.5% Rheotech 4800 had near-perfect suspension of Minex 12. The 1.0% Rheotech sample was a bit lower in overall optical performance and the 1.5% Rheotech 4800 sample aggregated and gelled up. At the 1.5% concentration, it is possible that as acrylate groups of the Rheotech copolymer are converted into salt by a base, they interact strongly with water molecule to occur the gelation.

In shown in the Figure 17, a partial sample loss was also observed in all the optimized samples during the heat-age. The amount sample loss was as high as 18g. It was hard to conclude that the sample loss was only water as PUD resin itself was supplied with only 36.5% non-volatile.

Figure 11. Separation Layers of Spuncoat PUD Samples After Heat Aging.

Among the eight final optimization samples, a PUD sample containing combination of 0.8% Byk 425 and 3% Aquatix 8421 yielded the best optical properties (98.90% optical clarity, 91.8 gloss at 60°, and 1.97% haze) (unmodified Minex 12 PUD formula: 96.9% clarity, 94.4 gloss at 60°, and 3.73% haze). Although this sample lacked perfect suspension of Minex 12, it exhibited soft pack characteristics after heat aging, and ease of remixing. High low-shear viscosity (~3500 cP) may be a drawback for coating formulators.

For formulators seeking a more perfect suspension or minimal separation, the formulation with Rheotech at 1.0% is the best option, Table 11. It provides near-perfect Minex 12 suspension with a lower-viscosity rheology profile. Although this PUD formulation option provides a slightly lower optical quality, these properties are less affected by heat aging.

Table 11. Formula of 1.0% Rheotech 4800 Optimized PUD Formula

Item	Wt. (g)
Charge under agitation	
Bayhydrol UV VP LS 2317	67.45
Irgacure 500	1.00
Mix 5 min, @ 900rpm	
Minex 12 slurry with 8% Solsperse 46000	7.08
DI Water	18.13
Mix 10 min @ 1100rpm	
1% Rheotech 4800	1.00
Mix 10 min, @ 1600 RPM	
Total	95.1
Total solid wt.	34.3
NVM %	17.18
% Minex 12 Solids	15.04

4 CONCLUSIONS AND RECOMMENDATIONS

The stability of nepheline syenite in an aqueous UV-cured PUD coating was attempted with NS (d50=1.7 μ m) at 15% solids utilizing dispersants, suspending aids, and rheology modifiers. Solsperse 46000 was the best dispersant aid among the five candidates. Rheology modifiers were essential to increase the low-shear viscosity of the PUD starting-point formula to help stabilize and suspend micron-sized nepheline syenite fillers in low-viscosity aqueous systems. The optimal optical was obtained in a sample optimized with a combination of 3.0 % Aquatix 8421 and 0.8% Byk 425; however it yields high low-shear viscosity (3500cP). Near perfect suspension of NS in the PUD system was given by 1.0% Rheotech 4800 with fair optical properties.

It is recommended that suspension of NS and optical properties of the PUD system can be improved significantly if finer NS particle sizes (e.g. d50=1.0 μ m or d50=0.5 μ m) are used. Rheology additives from Rheotech series should be considered in future work.

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5 APPENDIX A

Table 12. Dispersant Candidate

Dispersant	Chemistry	Supplier
Zephrym PD 3300B	Anionic polymeric dispersant (Proprietary)	Croda
Zephrym PD 4974	(Proprietary)	Croda
Solsperse 46000	Polymeric hyper-dispersant (Proprietary)	Lubrizol
DISPERBYK 2010	Acrylate copolymer with amine content (emulsion)	Byk
DISPERBYK 2015	Acrylate copolymer (solution)	Byk

Table 13. Suspending Aid Candidates

Suspending Aid	Chemistry	Supplier
Anti-terra 250	Solution of an alkylolammoinium salt of a high molecular weight acidic polymer	Byk
Byk 425	Solution of a modified urea modified polyurethane	Byk
Laponite EP	Natural layered silicate	Southern Clay Products
Laponite RD	Synthetic layered silicate	Southern Clay Products

Table 14. Rheology Modifier Candidates

Rheology Modifier	Chemistry	Supplier
Aquatix 8421	Non-ionic emulsion of a modified ethylene- vinyl- acetate copolymer wax	BYK
Disparlon AQH-800	Hybrid associative/non-associative amide based rheology modifier	Kusumoto Chemicals
Dsx 3291	Hydrophobically modified polyethylene oxide urethane	Cognis
Acrysol RM 2020	Hydrophobically modified polyethylene oxide urethane (Non-ionic)	Dow
Acrysol RM 825	Hydrophobically modified polyethylene oxide urethane (Non-ionic), Brookfield viscosity= 1000-2500 cps	Dow
Optigel WX	Organically modified and activated smectite product	Southern Clay Products
PolyPhobe 106HE	Acrylic copolymer in aqueous dispersion	Coatex
Rheotech 4800	Acrylic Associative thickener	Coatex

ASTM D869-85: Rating of Degree of Settling of Paint

10= Perfect suspension. No change from the original condition of the paint.

8= A definite feel of settling and a slight deposit brought up on spatula. No significant resistance to sidewise movement of spatula.

6= Definite cake of settled pigment. Spatula drops through cake to bottom of container under its own weight. Definite resistance to sidewise motion of spatula. Coherent portions of cake may be removed on spatula.

4= Spatula does not fall to bottom of container under its own weight. Difficult to move spatula through cake sidewise and slight edgewise resistance. Paint can be remixed readily to a homogeneous state.

2= When spatula has been forced through the settled layer it is very difficult to move spatula sidewise. Definite edgewise resistance to movement of spatula. Paint can be remixed to a homogeneous state.

0= Very firm cake that cannot be reincorporated with the liquid to form a smooth paint by stirring manually.

6 APPENDIX B

Pictures of Heat-aged Samples Optimized with Rheology Additives Only

2weeks 4weeks 2weeks 4weeks
 8% Solsperse4600+0.8% Byk425+2% Aquatix84218 8% Solsperse46000+0.8% Byk425+3% Aquatix8421

8% Solsperse4600+1.5% Byk425+3% Aquatix8421

8% Solsperse4600+4% Acrysol RM825

8% Solsperse4600+1% Rheotech4800

8% Solsperse4600+3% Acrysol RM825

8% Solsperse4600+5% Acrysol RM825

8% Solsperse4600+1.5% Rheotech4800

----- Boundary between two separation layers

7 APPENDIX C

Table 15. Results of Interactions between Aquatix8421 with Suspending Aids

Design	Suspending Aids	Initial		After Heat-aging for 7 days					
		Visual Clarity	Gloss 60 Day 0	Gloss 60 Day 7	Syneresis (mm)	Settling Rating	Package Stability	Ease of Remix	Comments
-1,-1	Ani Terra 250	Yes	92.3	79.4	29	0	Hard	No	Non-Homogeneous Remix
-1,+1		Yes	92.5	No Draw Down	33	0	Hard	No	Non-Homogeneous Remix
0,0		Yes	69.6	56.1	9	9	Soft	Yes	-
+1,-1		Yes	82.0	73.9	5.5	9	Soft	Yes	-
+1,+1		Yes	87.8	80.1	21	8	Soft	No	Non-Homogeneous Remix
-1,-1	Byk 425	Yes	87.0	88.2	21	9	Soft	Yes	-
-1,+1		Yes	84.0	87.5	0	10	Soft	Not Required	Not Pourable
0,0		Yes	86.0	88.0	0	10	Soft	Not Required	Not Pourable
+1,-1		Yes	82.7	85.9	0	9	Soft	Yes	Not Pourable
+1,+1		Yes	84.0	86.3	0	10	Soft	Not Required	Not Pourable
-1,-1	Laponte EP 2.5% Solution	Yes	92.3	79.4	29	0	Soft	No	Non-Homogeneous Remix
-1,+1		Yes	64.3	40.9	25	9	Soft	Yes	Flocculate
0,0		No	63.2	55.1	32	9	Soft	Yes	Flocculate
+1,-1		Yes	82.0	73.9	31	9	Soft	Yes	-
+1,+1		No	62.2	46.3	35	10	Soft	Yes	Not Pourable

Table 16. Results of Interactions between Acrysol RM825 with Suspending Aids

Design	Suspending Aids	Initial		After Heat-aging					
		Visual Clarity	Gloss 60	Gloss 60	Syneresis (mm)	Package Stability Rating	Sediment Packing Type	Ease of Remix	Comments
-1,-1	Anti Terra 250	Yes	86.6	88.5	30	8	Soft	Yes	-
-1,+1		Yes	86.0	89.9	32	9	Soft	Yes	-
0,0		Yes	87.3	No Draw Down	28	8	Soft	Yes	Not Pourable
+1,-1		Yes	85.9	No Draw Down	10	9	Soft	Yes	Not Pourable
+1,+1		Yes	87.6	No Draw Down	6	8	Soft	Yes	Not Pourable
-1,-1	Byk 425	Yes	86.1	No Draw Down	28	7	Soft	No	Not Pourable, Non-Homogeneous Remix
-1,+1		Yes	85.2	88.6	9	9	Soft	Yes	Not Pourable
0,0		Yes	85.1	No Draw Down	13	7	Soft	No	Not Pourable, Non-Homogeneous Remix
+1,-1		Yes	86.8	No Draw Down	10	8	Soft	Unknown	Jar Broken & Sample Lost
+1,+1		Yes	82.0	88.2	3	9	Soft	Yes	Not Pourable
-1,-1	Laponite EP 2.5% Solution	Yes	86.6	88.5	4	8	Soft	Yes	-
-1,+1		Yes	73.9	77.8	11	9	Soft	Yes	Not Pourable
0,0		Yes	82.9	87.9	10	9	Soft	Yes	Viscous
+1,-1		Yes	85.9	87.0	10	9	Soft	Yes	Viscous, Non-Homogeneous Remix
+1,+1		Yes	80.1	82.2	4	10	Soft	Not Required	Not Pourable

Table 17. Results of Interactions between Acrysol RM825 and RM2020, and Suspending aids

Design	Suspending Aids	Initial		After Heat-aging for 7 days					
		Visual Clarity	Gloss 60	Gloss 60	Syneresis (mm)	Package Stability Rating	Sediment Packing Type	Ease of Remix	Comments
-1,-1	Anti Terra 250	Yes	91.4	91.9	31	6	Hard	Yes	Smoother Caste Film
-1,+1		Yes	92.2	92.8	34	8	Soft	Yes	Smoother Caste Film
0,0		Yes	87.9	89.7	32	8	Soft	Yes	Smoother Caste Film
+1,-1		Yes	87.3	No Draw Down	22	8	Soft	No	Not Pourable, Non-Homogeneous Remix
+1,+1		Yes	90.7	91.7	12	9	Soft	Yes	Not Pourable
-1,-1	Byk 425	Yes	86.6	88.9	29	9	Soft	Yes	Not Pourable
-1,+1		Yes	88.6	No Draw Down	10	9	Soft	No	Not Pourable, Non-Homogeneous Remix
0,0		Yes	86.8	No Draw Down	17	2	Soft	No	Not Pourable, Non-Homogeneous Remix
+1,-1		Yes	88.6	No Draw Down	10	9	Soft	No	Not Pourable, Non-Homogeneous Remix
+1,+1		Yes	85.7	No Draw Down	10	9	Soft	No	Not Pourable, Non-Homogeneous Remix
-1,-1	Laponite EP 2.5% Solution	Yes	91.4	91.9	31	6	Hard	Yes	-
-1,+1		Yes	70.9	71.5	20	9	Soft	Yes	-
0,0		Yes	83.5	85.7	27	9	Soft	Yes	Not Pourable
+1,-1		Yes	87.3	No Draw Down	22	8	Soft	No	Not Pourable, Non-Homogeneous Remix
+1,+1		Yes	80.9	81.9	5	9	Soft	Yes	Not Pourable

Table 18. Results of Study of Effect of Solsperse 46000 Concentration

Design	Day 0					Day 14										
(Solsperse 46000, Acrysol825)	Optical Clarity	Haze	Gloss 60°	pH	Visc @ 100rpm	Optical Clarity	Haze	Gloss 60°	Visc @ 100rpm	pH	Sediment Layer (mm)	Sediment Packing Type	Package Stability Rating	Ease of Remix	Syneresis Layer (mm)	
None (Control)	96.9	3.7	94.40													
0,0	95.70	5.7	87.20	7.1	280	98.80	1.61	92.80	500	-0.46	17	Soft	8	Yes	41	
+1,-1	97.10	6.5	89.20	7.1	550	98.60	2.50	92.00	550	-0.47	5	Semi-Hard	7	Yes	60	
-1,-1	96.00	6.1	88.00	7.2	555	98.10	3.53	91.90	650	-0.56	5	Soft	8	Yes	55	
-1,+1	96.20	6.5	86.80	7.1	700	98.60	3.10	91.50	1000	-0.44	30	Soft	8	Yes	35	
+1,+1	96.50	6.5	87.80	7.2	500	98.70	2.56	92.50	500	-0.35	34	Soft	8	Yes	29	
0,0 (2)	96.00	6.4	88.60	7.0	500	98.60	2.20	92.00	500	-0.43	20	Soft	8	Yes	44	
0,+1	95.90	6.4	87.50	7.1	Gel	98.40	2.76	92.10	700	-0.32	23	Soft	8	Yes	30	
0,-1	95.90	5.8	88.90	7.0	550	97.90	2.70	91.60	550	-0.32	5	Soft	8	Yes	60	
-1,0	95.90	6.8	87.60	7.1	510	98.90	1.92	91.90	510	-0.22	10	Soft	8	Yes	48	
+1,0	96.60	5.9	88.60	7.0	550	98.60	2.20	92.50	550	-0.32	15	Soft	8	Yes	49	

Table 19. Study of Interactions of a Dispersant, Rheology Modifier, and Suspending Aid

Design	Day 0					Day 14									
(Solsperse 4600, Byk425, Aquatix8421)	Optical Clarity	Haze	Gloss 60°	pH	Vis @ 100rpm	Optical Clarity	Haze	Gloss 60°	Vis @ 100rpm	•pH	Sediment Layer (mm)	Sediment Packing Type	Package Stability Rating	Ease of Remix	Syneresis Layer (mm)
None (Control)	96.9	3.73	94.4	7.07	40										Top
-1,-1,-1	95.60	5.21	92.30	6.59	85	Flocculate					9	Soft	8	Yes	56
+1,-1,-1	96.60	7.28	89.00	6.89	Gel	Flocculate					10	Soft	8	Yes	57
-1,+1,-1	96.40	8.11	76.20	6.86	Gel	98.40	21	90.70	500	-0.10	21	Soft	8	Yes	46
+1,+1,-1	96.40	6.71	83.10	6.32	188	98.50	21	91.30	500	+0.47	21	Soft	8	Yes	46
-1,-1,+1	95.70	7.81	83.40	6.66	109	Flocculate					7	Soft	8	No	63
+1,-1,+1	96.00	8.52	83.60	6.69	Gel	Flocculate					5	Soft	8	No	64
-1,+1,+1	84.50	10.30	81.90	6.82	Gel	97.90	16	89.70	500	+0.17	16	Soft	8	Yes	25
+1,+1,+1	87.20	6.40	85.70	7.03	Gel	98.50	6	91.30	500	-0.26	6	Soft	8	Yes	30
-1,0,0	96.30	6.31	88.60	6.94	Gel	98.50	1.70	92.40	550	-0.15	17	Soft	8	Yes	50
0,0,0	96.20	6.97	88.20	6.94	Gel	98.10	2.72	91.10	550	+0.05	16	Soft	8	Yes	43
+1,0,0	96.70	6.75	88.10	6.92	500	98.80	2.13	93.30	700	-0.18	16	Soft	8	Yes	44
0,-1,0	96.50	7.25	87.10	6.89	99	Flocculate					18	Soft	8	No	48
0,+1,0	90.00	7.09	86.70	6.88	Gel	99.00	2.21	93.00	700	-0.23	20	Soft	8	Yes	33
0,0,-1	95.70	6.77	87.10	7.06	500	99.10	1.85	92.70	550	-0.23	23	Soft	8	Yes	43
0,0,+1	95.10	7.81	86.20	6.86	500	99.30	1.57	91.80	550	-0.20	13	Soft	8	Yes	40

Table 20. Results of PUD Samples Optimized with Rheology Additives

					Day 0										
Solsperse 46000 %	Byk 425 %	Aquatix 8421 %	Acrysol 825 %	Rheotech 4800 %	Optical Clarity	Haze	Gloss 60°	Viscosity at 100rpm	pH	Sediment Layer (mm)	Sediment Packing Type	Package Stability Rating	Ease of Remix	Syneresis Layer (mm)	Comments
8	None (Control)				97.0	1.79	94.4	40	7.07	Not necessary to collect for Day 0					
	0.8	2			96.4	8.18	86.1	550	6.90						
	0.8	3			95.9	8.04	85.8	525	6.96						
	1.5	3			96.0	8.32	84.7	550	6.99						
			3		96.7	3.74	87.1	510	7.20						
			4		96.5	5.81	87.3	550	7.30						
			5		97.2	6.77	87.1	550	7.27						
				1	95.2	6.01	86.6	550	7.04						
				1.5	95.0	7.52	84.2	520	6.76						
					Day 14										
									• pH						
	0.8	2			98.2	2.54	94.4	550	-0.11	29	Soft	8	Yes	32	
	0.8	3			97.3	3.87	93.4	550	-0.17	34	Soft	8	Yes	25	
	1.5	3			97.8	4.55	93.8	550	-0.20	20	Soft	8	Yes	37	
			3		98.2	6.10	93.5	550	-0.41	27	Soft	8	Yes	30	
			4		98.2	5.05	93.0	550	-0.51	36	Soft	8	Yes	18	
			5		94.5	6.06	88.1	320	-0.48	0	None	10	Yes	57	
				1	Localized Gelation				-0.25		None	10	0	57	Localized Gelation
					1.5	Day 28									
	0.8	2			96.5	2.98	87.7	550	-0.41	14	Soft	8	Yes	50	
	0.8	3			98.8	1.97	92.3	550	-0.25	7	Soft	8	Yes	54	
	1.5	3			98.9	2.38	91.3	550	-0.29	7	Soft	8	Yes	54	
			3		98.8	2.83	91.8	550	-0.31	6	Soft	8	Yes	54	Specks throughout Day14 and 28 films
			4		98.7	4.47	92.6	550	-0.52	7	Soft	8	Yes	50	
			5		98.8	5.16	93.4	550	-0.60	6	Soft	8	Yes	52	
				1	95.4	6.67	84.6	165	-0.41	0	Soft	9.5	Yes	54	
				1.5	Localized Gelation				-0.17	0	None	10	No	54	Localized Gelation

PART II ABSTRACT

VISCOSITY STABILIZATION OF TINTED LATEX ARCHITECTURAL COATINGS

MAUNG YE HTET

Associative thickeners are sensitive to surfactant concentration in waterborne pastel base coatings. When a highly surfactant concentrated colorant is added, the surfactant disrupts the thickening mechanism of the associative thickeners, which lowers the viscosity of the coating significantly. The pastel base coatings are generally formulated to have viscosities around 100 KU. After addition of the colorants, the coating's viscosity is reduced by 30-38 KU. The loss in viscosity negatively impacts the rheology properties of waterborne architectural coatings that require a high viscosity (e.g., $10^1 - 10^3$ Pa. s) under low shear rates (e.g., $10^{-3} - 10^{-1}$ s⁻¹) is required to control the settling, sagging, leveling and the film thickness. In this research project, five latex emulsion pastel base coatings were prepared with five different lower-shear viscosity (KU) builders (one cellulosic thickener, and four associative thickeners), but one high-shear viscosity (ICI) builder, cellulosic thickener, is used in all the coatings. Seven low-VOC Universal colorants were used. The rheology characteristic of these coatings before and after addition of the coating is investigated.

Cellulosic thickener showed no sensitivity to surfactants contained in colorants. Newly developed associative thickener showed viscosity stabilization in high shear rate regions although it is sensitive to colorants at low shear rates. No major variation in tint strength was observed in tinted pastel bases. Tint strength does not appear to depend upon the types of thickeners.

PART II

8 INTRODUCTION

8.1 Acrylic emulsion latex

Natural latex is found in the inner layer of the cortex of certain trees (H. Stevens and W. Stevens 1936). Materials made from natural latex have been used in many applications for over a thousand years. During World War II, materials, especially rubber made from natural latex, became an essential commodity for military uses for the countries that were in the war (Wilson 1943). To keep up with the material demand, a process to synthesize latex was needed. In the mid-1900s, the emulsion polymerization technique was developed for synthesizing the latex materials (Wilson 1943). Since then the technique has been widely used to make resins used in coatings, adhesive and sealants.

According to a study conducted by the consulting firm Kusumgar, Nerlfi & Growney, 3.9 billion pounds architectural coatings worth \$9.1 billion was consumed in the United States in 2011. Architectural coatings are generally available in three different qualities: good, better, and best (Z. Wicks et al. 2007). The best paints are formulated to provide the longest service life with good coverage (Z. Wicks et al. 2007). The majority of the architectural coatings are formulated without colorants so that they can be tinted at the point of sale with any desired colorants. A variety of architectural coatings are available for the architecture market: exterior house paint, interior flat wall paint, gloss enamels, and more (Z. Wicks et al. 2007).

A general overview of exterior house paint is discussed in this paper since this type of coating was used for this research project. The vast majority of exterior and interior house paints sold in the United State are waterborne latex paints whose resin is produced by emulsion polymerization. Water being the paint's vehicle not only significantly reduces the VOC content but also produces products meeting EPA and other regulatory requirements. Blistering in the latex paints is unusual due to their high moisture vapor permeability. High quality latex paints are also

more resistant to cracking and chalking than alkyd paints, especially on wood substrates (Z. Wicks et al. 2007). However, it has been found that leveling of latex paints is generally not as good as that of the solvent borne paints (Z. Wicks et al. 2007). It is not recommend applying the latex paints on contaminated or chalky paint surfaces as they lead to poor adhesion (Z. Wicks et al. 2007).

8.2 Emulsion Polymerization

An emulsion is a stable dispersion of liquid in liquid, whereas a latex is a stable dispersion of polymer solids in water. The emulsion polymerization technique is used to synthesize latex. A latex preparation includes hydrophobic monomers, water-soluble initiator, water, and surfactant. The monomer forms large droplets in water stabilized by the surfactant molecules. Above the critical micelle concentration (CMC), an excess of the surfactant molecules gather to form micelles in small rod-like or spherical structures containing 50 to 100 surfactant molecules (Fried 2003). The structure of micelle formation depends upon the nature of the surfactant (Fried 2003).

For polymerization to occur, monomer molecules dissolved in water need to migrate into the micelles first. Polymerization is initiated when the initiator reaches into the monomer containing micelles. The monomer molecules are transferred from the droplets to the micelles as the polymerization continues until the droplets are depleted and the swollen micelles are transformed into large polymer particles with 50 to 1000 nm in diameter (Fried 2003). The stable dispersion of these polymer particles in water is called a latex.

8.3 Rheology

Rheology is the science of flow and material deformation under the influence of applied forces. It is crucial to understand rheology in coating formulation, and understanding it allows coating formulators to achieve the desired rheological properties for coating applications. How much a liquid flows depends on its viscosity, the ratio of shear stress to shear rate.

$$\eta = \frac{\tau}{\dot{\gamma}}$$

η = Viscosity (Pa.s)
 = Shear stress (Pa)
 $\dot{\gamma}$ = Shear rate (s^{-1})

Shear stress is defined as a ratio of the applied force to the area the force acts on.

$$\tau = \frac{F}{A}$$

= Shear stress
 F = Force (N)
 A = Area (m^2)

Figure 18. Shear Deformation due to an Applied Force

The model shown in Figure 18 can be used to define the shear rate ($\dot{\gamma}$). The upper plate can be moved while the lower plate is stationary. Layers of liquid separate the two plates. When the force (F) is applied to the upper plate with an area (A), the plate moves forward with velocity (v). The upper plate moves with the velocity (v), but the velocity decreases approaching the stationary plate creating a velocity gradient (v/h). If the gradient is constant over a section of the liquid, it equals v/h . This ratio is defined as shear rate.

$$\dot{\gamma} = \frac{v}{h}$$

$\dot{\gamma}$ = Shear rate (s^{-1})
 v = velocity (m/s)
 h = height (m)

8.3.1 Viscosity Profiles

There are three main types of time-independent viscosity profiles: Newtonian, shear thinning and shear thickening, as shown in Figure 19. In a Newtonian profile, the viscosity is constant under any shear rate. A profile where the viscosity decreases with increasing shear rate is called shear thinning. Shear thickening results when the viscosity increases with increasing shear rate.

Figure 19. Time Dependent Viscosity Profiles
(Specialties 2008)

If the system shows a time-dependent viscosity profile, the system can be either thixotropic or anti-thixotropic. Here the viscosity decreases with time under a constant shear rate. The viscosity decreases as the thixotropic structure broken down under shear (Figure 20, black profile). The viscosity increases with decreasing the shear (red profile), but it requires some period of time to recover the structure after shear is removed.

Figure 20. Viscosity Profiles of Thixotropic System
(Specialties 2008)

8.4 Thickeners

Thickeners, additives also known as rheology modifiers, are required in waterborne coatings to obtain rheology profiles that suit coating applications and optimize overall coating properties. Rheology additives such as clays, plant exudates and natural or synthetic polymeric thickeners are generally used to increase the liquid viscosity, to suspend dispersions of additives in the liquid and to improve the stability of the dispersion under temperature and extreme shear (Davison and Lane 2003). In this project, cellulosic (e.g. HEC (hydroxyl ethyl cellulose)) and associative type thickeners (e.g. HEUR (Hydrophobically Modified Ethoxylated Urethane)) are used for latex coatings formulations. Their typical viscosity profiles are exhibited in Figure 21.

Figure 21. Viscosity Profiles of Cellulosic and Associative Thickeners

8.5 HEC Thickeners

HEC (hydroxyl ethyl cellulose) thickeners are traditional cellulosic thickeners with high molecular weights. These types of thickeners are composed of a series of anhydroglucose units with 1,4 linkages (Figure 22).

Figure 22. HEC Type Thickener
(Davison and Lane 2003)

Each unit contains three hydroxyl groups that can be substituted with ethers under etherification. The thickening mechanism occurs via hydrogen bonding between the hydrophilic polymer backbone and water molecules. This hydrogen bonding expands the hydrodynamic volume of the polymers. The volume expansion occupies a large proportion of available free space, and restricts free movement of latex particles, pigments, and fillers or extenders in the coating system to raise the viscosity of the coating. In addition, the increase in viscosity is due to chain entanglements of the thickener polymer molecules and depletion flocculation when polymer molecules are not absorbed on the particles (Figure 23).

Hydrogen Bonding Network

Chain Entanglement

Figure 23. Thickening Mechanism of HEC Thickeners
(Davison and Lane 2003)

The thickening efficiency is a function of its concentration. At critical polymer concentration, the chains entangle to increase the viscosity very effectively. HECs are inexpensive, however, they can lead to poor leveling, reduction of gloss, syneresis, and biodegradation (Davison and Lane 2003). Another drawback is that since HECs are supplied in powder form, it is necessary to prepare a solution of the thickeners with water at low percentage. Further, if the coatings are formulated with HECs, it is difficult to adjust the viscosity after formulation.

8.6 HEUR Thickeners

Over the past thirty years, HEUR type thickeners were introduced to replace traditional HEC type thickeners (Davison and Lane 2003). These types of thickeners are known as associative thickeners composed of a hydrophilic polyethylene glycol segment in the middle with hydrophobic groups at the end of the thickener's structures (Figure 24). Possible association modes of these thickeners include association with themselves, pigments, surfactants and latex particles via hydrophobic groups (Figure 25).

Figure 24. HEUR Type Associative Thickener

Figure 25. Thickening Mechanism of HEUR (Associative Thickeners)

HEURs improve coatings' leveling and spreading, compatibility with latexes and colorants, and resistance to bacterial attack (Davison and Lane 2003). However, they are sensitive

to latex particle characteristics, surfactant, dispersants, co-solvents, and other ingredients in coatings. HEUR thickeners have lower molecular weight than HECs. Hydrophobically modified Aminoplast Ether (HEAT) is another type of associative type thickener used for one of the formulations in this project.

8.7 Effect of Colorant Addition

Colorants are supplied with high surfactant concentrations to stabilize the pigment particles. After addition of the colorants, extra surfactants can occupy and displace adsorbed thickeners at the latex surface. This occupation removes some of the adsorbed thickeners that associate with other components to build networks. The replacement disassociates the networks to lower viscosity. The mechanism of viscosity loss upon colorant addition is displayed in Figure 26.

Figure 26. Mechanism of Viscosity Loss upon Tinting/ Addition of Colorants

9 EXPERIMENTAL MATERIALS AND METHODS

9.1 Pastel Paint Formulation

Sufficient amount of pigment grind was prepared for total five formulations (Table 21). Pigment grind was ground to Hegman Fineness of Grind value of 7. Then Let-down ingredients, except KU builder, were added to the pigment grind. KU builder is a term used in industry to describe a thicker that increases low-shear viscosity. The batch of mixture of pigment grind and Let-down was proportionally divided into five formulations. Then five different KU builders were added into the five different formulations (Table 22).

Table 21. ICI Builders and KU Builder used for Formulations

Thickeners	Type	Chemistry	Supplier	Weight % Solid
Natrosol 250GR	ICI Builder ¹	HEC	Ashland	4.00 ³
Natrosol 250HR	KU Builder ²	HEC	Ashland	2.00 ³
Acrysol RM 995	KU Builder	HEUR	Dow	23.50
Rheovis PU1191	KU Builder	HEUR	BAF	30.00
Optiflo-TVS	KU Builder	HEAT	Southern Clay	30.00
Acrysol SCT275	KU Builder	HEUR	Dow	17.50

¹KU builder is a thicker used to increases low-shear viscosity

²ICI builder is a thicker used to increases high-shear viscosity

³Solution in water

Table 22. Pastel Base Paint Formulations with Different KU Builders

	KU Builders					Chemical Function
	Natrosol 250HR	Acrysol RM-995	Rheovis PU1191	Optiflo-TVS	Acrysol SCT275	
Thickener Chemistry	HEC	HEUR	HEUR	HEAT	HEUR	
Grind (g)						
Water	15.88	17.69	18.57	18.57	22.40	Aqueous Medium
Natrosol 250GR	17.73	19.76	20.74	20.74	25.10	ICI builder
Tamol 850	1.49	1.66	1.75	1.75	2.20	Dispersant
BYK-348	0.64	0.71	0.74	0.74	0.90	Surfactant
BYK-023	1.27	1.42	1.49	1.49	2.60	Surfactant
Nuosept 95	0.95	1.06	1.11	1.11	1.40	Biocide
Minex-10	3.18	3.54	3.71	3.71	4.50	Nepheline Syenite
TiPure R902	73.98	82.44	86.52	86.52	104.20	TiO ₂
Let-Down (g)						
EPS-2757	141.88	158.09	165.91	165.91	201.00	Acrylic latex
Water	0.00	57.80	58.40	55.20	52.10	Aqueous Medium
Propylene Glycol	1.40	1.56	1.63	1.63	1.90	Free-thaw agent
Texanol	2.84	3.16	3.32	3.32	4.10	Coalescing aid
BYK-023	2.55	2.84	2.98	2.98	2.80	Surfactant
Ammonium Hydroxide	0.31	0.35	0.36	0.36	0.50	Used for pH adjustment
Natrosol 250GR	36.91	41.13	43.16	43.16	50.10	ICI builder
KU Builder	55.00	7.20	6.10	8.70	4.20	KU builder
Total Weight (g)	356.00	400.40	416.50	415.90	499.80	
%Solids by Weight	43.29	43.00	43.40	43.65	44.58	
%Solids by Volume	31.83	31.15	31.50	31.79	32.84	
PVC	21.99	21.90	21.89	21.74	21.13	
Density (lb/gal)	10.54	10.37	10.39	10.40	10.41	

9.2 Tinting

Seven colorants were used for tinting the five pastel bases thickened with five different thickeners (Table 21). The colorants belong to the 1900 Universal Colorants series from the Color Corporation of America (Table 23). Five grams of colorant were added to 40 grams of base paint (20 oz./ gal) and mixed in a Thinky Mixer AR-100 for 2 minutes. Samples were then transferred to 4 oz. jars for tint strength and rheology analysis.

Tint strength of the tinted pastel bases was determined according to the procedure described in ASTM D4838-88. Drawdowns were prepared with a 6 mil drawdown bar.

Table 23. Colorants used for Tinting

Color ID	Color
1913	Yellow
1921	Phthalo Green
1932	Phthalo Blue
1935	Red Oxide
1977	Yellow Oxide
1982	Magenta
1991	Lamp Black

9.3 Rheology Characterization

9.3.1 Krebs Units (KU) Viscosity Measurement

KU viscosity of the pastel base coatings was measured immediately after mixing and after twenty-four hours using a Stromer Viscometer from Brookfield Engineering Laboratories.

9.3.2 Rheology Characterization with Rheometer

Rheology characterization was performed using a TA Instruments Discovery HR-2 rheometer equipped with a 40mm, 2° cone. The gap between the cone and Peltier plate was set at 55µm. The rheometer was operated at 25°C. Samples were stirred gently for about 5-10 seconds with a spatula before loading. To obtain the viscosity profiles the instrument was run in a steady-state flow mode from 0.01-1000s⁻¹ shear rate with a maximum equilibration time of 180 seconds.

10 RESULTS AND DISCUSSION

10.1 Percent Solids by Weight and Stormer Viscosity of Pastel Bases

The percent solids by weight and Stormer/ KU viscosity of pastel bases are shown in Table 24. The pastel bases are formulated to have a percent solids by weight closed to 44%. Stormer viscosities of the HEUR-thickened pastel bases are higher than that of the HEC-thickened pastel base and above 90 KU target.

Table 24. Percent Solids by Weight and KU Viscosity of Pastel Bases

Chemistry of Thickeners	Thickeners	% Solids by Weight	Initial Stormer Viscosity (KU)	24 Hours Stormer Viscosity (KU)
HEC*	Natrosol 250HR	43.2	86	87
HEUR**	Acrysol RM-995 ⁺	42.5	87	92
HEUR**	Rheovis PU1191	43.3	90	94
HEAT**	Optiflo-TVS	44.8	95	101
HEUR**	Acrysol SCT-275	43.1	92	98

⁺Newly developed associative thickeners promise to minimize the viscosity loss upon colorant addition.

* Cellulosic Type Thickener

** Associative Type Thickener

10.2 Viscosity Profile of Pastel Bases

Viscosity profiles of untinted pastel bases are shown in Figure 27. Typically, the viscosity of HEC-thickened pastel bases at low shear (10^{-2} s^{-1}) is higher than that of HEUR-thickened pastel bases. However, it is interesting to see that viscosity of PU1191 and Acrysol SCT 275 (Associative) thickened base pastel bases are as high as the Natrosol HR250 (HEC) thickened sample. However, since the amount of thickener added was varied in all the formulations, it cannot be concluded that those two HEUR thickeners and the HEC thickener perform equally at the low shear rate before tinting.

Figure 27. Viscosity Profiles Untinted Pastel Bases Thickened With Five Different Thickeners

A dramatic viscosity drop in HERU-thickened pastel bases is observed around $5\text{--}10\text{ s}^{-1}$ shear rate. This viscosity drop is due to disassociation of thickening mechanism between the HERU thickeners and other components in the coating under the shear rate.

10.3 Effect of Addition of Colorants on Viscosity of Pastel Bases

Viscosity profiles of HEC-thickened and HEUR-thickened samples with colorants are shown in Figure 28 and Figure 29-32, respectively. As expected no viscosity loss was observed in tinted HEC (Natrosol HR 250)-thickened samples (Figure 28), which indicates the lack of sensitivity of HEC thickeners to the colorants.

Figure 28. Viscosity Profiles Of Tinted HEC Thicken Pastel Bases

However, viscosity profiles in Figure 29-32 illustrate the sensitivity of associative thickeners to the colorants. No viscosity drop was observed in some tinted HEUR thickened samples. Among the seven tinted Acrysol RM 995 (HEUR)-thickened samples, no viscosity drop was found in the samples tinted with the following colorants: 1977 Yellow Oxide, and 1921 Phthalo Green (Figure 29). Even a viscosity increase was found in the 1921 Phthalo Blue tinted sample. It was possible that the surfactant concentration in the Phthalo Blue colorant was low but it was concentrated enough to reach CMC region and increase the viscosity of coating. The viscosity dependence of surfactant concentration (Figure 33) in similar systems is reported in (Manion 2011), (Dai 2001), (Dakota 2001), (Yekta 1993), (Kostansek 2003), and (Richard 1997).

The increase in viscosity could be also caused by pigment flocculation in the sample. Due to the high surfactant contents in the other colorants, viscosity dropped in the other Acrysol RM995-thickened samples. Among the tinted Optiflo-TVS (Associative HEAT type)-thickened samples, only the Phthalo Blue tinted sample can retain the initial viscosity (Figure 31). This observation seems to support the previous assumption surfactant concentration of the Phthalo Blue is lower than that of the others. A significant viscosity drop was observed in all the Acrysol SCT275 and PU 1191-thickened pastel bases upon tinting.

Figure 29. Viscosity Profiles Tinted Acrysol RM995 Thickened Pastel Bases

Tinted samples thickened with Acrysol RM995 have similar viscosity profiles to the un-tinted samples when the shear rate reaches above 0.5 s^{-1} . Acrysol RM995 is a newly developed associative thickener, and its supplier claims that the thickener is engineered to retain its initial KU viscosity upon tinting. KU viscosity of tinted samples was not collected due to the inadequate amount of samples. Even if they were known, KU viscosity alone does not provide complete information of the coatings' viscosity behaviors under high and low shear rates. KU viscosity can only be used to estimate the viscosity around 100 s^{-1} shear rate. According to the viscosity profiles provided by the Discovery HR-2 rheometer, it was observed that un-tinted and tinted Acrysol RM995 thickened samples seemed to have same viscosity around 100 s^{-1} shear rate. Therefore, the manufacturer's claim appears to be in true that the tinted samples had little to no KU viscosity loss upon tinting. However, in low shear region ($0.01 - 0.8 \text{ s}^{-1}$), viscosity dropped in some of the tinted samples. This observation indicates that although the thickener is designed to retain KU viscosity upon tinting, under the low shear it still has some sensitivity to surfactants

contained in the colorants. The thickening mechanism of this newly developed thickener is not fully understood at this moment. Its proposed thickening mechanism is explained in the literature (Saucy 2008). Unlike this newly developed thickener, viscosity drop upon tinting was observed at both high and low shear rate in all the tinted Acrysol SCT 275 (old generation associative thickener)-thickened samples (Figure 30). This observation indicates that the new developed Acrysol thickener has superior performance than the old generation Acrysol thickener.

Figure 30. Viscosity Profiles Tinted Acrysol SCT 275 Thickened Pastel Bases

Figure 31. Viscosity Profiles Tinted Optiflo-TVS Thickened Pastel Bases

Figure 32. Viscosity Profiles Tinted PU 1191 Thickened Pastel Bases

Figure 33. Viscosity Dependence Of Surfactant Concentration

10.4 Effect of Type of Thickener on Tinting Strength

Effect of type of thickener on tint strength of tinted pastel bases was studied using ASTM D4838-88. Complete hiding was achieved in all the tinted samples with contrast ratios above 98. Calculation of the tinting strength is possible due to complete hiding of the samples.

Figure 34. Tint Strength of Tinted Pastel Bases Thickened with Five Different Thickeners

The calculation procedure described in ASTM D4838-88 was used to determine the relative tinting strength of the seven colorants in the four associative thickeners, compared to the Natrosol base, which was set as the standard. Figure 34 illustrates a comparison of the relative tint strength of each colorant, relative to the Natrosol paint base, with 100 used as the standard for each tinted color using the Natrosol paint base. There is very little apparent change in the tint strength as differences are less than 5 percent, as indicated in the figure. It appears that tinting with 1932 (Phthalo Blue) has the greatest amount of variability in tint strength. The type of thickeners does

not seem to have effect on tint strength of tinted samples. The variation of tint strength seems to depend only upon the colorants.

The ASTM suggested colorant to pastel base ratio was 5g of colorant to 40 g of pastel base (20 oz./ gal). This concentration appears to be higher than the concentration described in the literature (Saucy 2008) which is 8 oz./gal (2g of colorant to 40g of pastel base). Reducing the colorant concentration will help retaining the initial KU viscosity, but tint strength of the tinted samples will probably reduced.

11 CONCLUSION AND RECOMMENDATIONS

In this research project, five latex coatings were prepared with five different lower-shear viscosity/ KU builders (one cellulosic thickener, and two new generation and two old generation associative thickeners), but one high-shear viscosity/ ICI builder, cellulosic thickener, is used in all the coatings. Cellulosic thickener showed no sensitivity to surfactant contained in colorants. Newly developed associative thickener showed viscosity stabilization in high shear rate regions although it is sensitive to colorants under low shear rates. No major variation in tint strength was observed in tinted pastel bases. Tint strength does not seem to depend upon the types of thickeners used.

Recommended future work includes understanding the thickening mechanism of newly developed thickener. Viscosity loss upon tinting should be further studied at lower colorant concentration to investigate how the concentration affects on the viscosity of pastel bases.

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