Phase Behaviors and Film Properties of Dispersions and Coatings Containing Associative and Conventional Thickeners

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SYNOPSIS

Phase-separation behaviors of latex dispersions, using commercial latices of three different median sizes, and pigmented coatings are examined. Both the dispersions and pigmented coatings at a 0.32 volume fraction of total dispersed phase were thickened with water-soluble polymers, with and without surfactant hydrophobes. Latex dispersions thickened with water-soluble polymers without hydrophobe modification follow the phase-separation behavior described by the volume restriction flocculation (VRF) concept (i.e., molecular weight of the thickener or particle size of the latex). This is surprising since commercial latices contain a variety of surface-stabilizing moieties, in addition to surfactant. Latex dispersions thickened with commercial and model hydrophobically modified ethoxylated urethane (HEUR) polymers do not follow the phase-separation behavior predicted by the VRF concept. The lack of correlation of phase behavior with latex median size in HEUR-thickened formulations led to an examination of four secondary thickeners, noted for providing high viscosities at low shear rates. With an all-acrylic, large median-size latex, the combinations of commercial HEURs with secondary thickeners are effective in eliminating phase separation; only partial reduction in phase separation is observed with a vinyl acetate-acrylic large-particle latex. The influence of HEUR/secondary thickener blends on the film properties also is discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The properties of water-borne latex coatings, from storage stability to application characteristics to final film performance, are related, in part, to the choice of thickener and its influence on the rheological behavior of the coatings at different shear rates. Hydroxyethyl or hydroxypropyl methyl cellulose have been, until recently, the major products controlling the rheological properties[1-4] of water-borne latex coatings. Two major problems are realized when cellulose ethers are used: (1) biodegradation of the thickener[5,6] and (2) spatter of the coating during application.[2-4,7-9] The latter occurs when small amounts of high molecular weight polymer are used. Hydrophobically modified, alkali-swellable emulsion (HASE) thickeners overcome these deficiencies, but alkali sensitivity of the dry film is observed.[10,11] Hydrophobically modified ethoxylated urethane (HEUR) thickeners improve coatings flow and leveling,[12,13] increase film gloss,[14] eliminate roll spatter, improve barrier properties, and reduce alkali sensitivity of the coatings.[10,11,15] Deficiencies, however, are observed in HEUR-thickened coatings. They are phase separation,[16] poor storage stability, poor sag resistance, and a strong sensitivity to changes in other formulation components.

The phase behavior of colloidal dispersions based on DLVO (Deryagin–Landau–Verwey–Overbeek) theory[17,18] has been extensively studied both theoretically and experimentally. In this theory, the potential energy of electrostatic repulsion, V_R, between the particles and the potential energy of the van der Waals attraction, V_A, are added to obtain the total potential energy of interaction, V_T ($V_T = V_R + V_A$).

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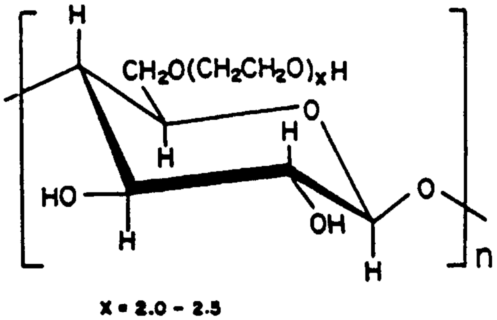
The form of the interaction potential energy curve as a function of particle separation distance determines colloid stability. The shape of the potential energy curve is a function of particle size, ionic charge density of the particle surface, and the ionic strength of the medium. Two general methods of imparting colloid stability are recognized: electrostatic and steric stabilization. Theories[19] on steric stabilization have been developed in recent years. A major difficulty encountered in applying the concepts to practical systems is that many parameters are experimentally unmeasurable, e.g., the segment density distribution in the adsorbed or attached layers and the number of segments per loop. Combination of the two mechanisms, electrosteric stabilization, also is recognized. The technology of the stabilization of the dispersed components in coating formulations is, to a large extent, empirical.

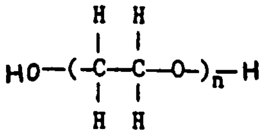
This study addresses some of the deficiencies encountered in HEUR-thickened dispersions. The syneresis of latex dispersions and of coating formulations containing various commercial latices thickened with commercial and model HEUR thickeners are examined. Complementary thickeners: HEC, HASE, microcrystalline cellulose (MCC), and attapulgite (ATT), are added to inhibit visible phase separation by increasing the viscosity at low shear rate, and the film properties of the applied formulations are evaluated.

SYMBOLS

VRF	volume restriction flocculation: When two particles approach, polymer chains located between the particles are squeezed out of the interparticle region since their insertion in the restricted space would otherwise cause a loss of polymer conformational entropy, resulting in a free-energy increase. The exclusion of polymer destroys the local osmotic balance, i.e., the polymer concentration between the particles is lower than that in the bulk. Osmosis then forces solvent to diffuse out of the interparticle space, resulting in an attraction between the particles. The process can lead to a phase separation, with one phase rich in polymers and the other rich in the dispersed phase.
HASE	hydrophobically modified alkali-swellable emulsion
HEC	hydroxylethyl cellulose [Fig. 1(a)]
HEUR	hydrophobically modified ethoxylated urethane (Fig. 2)
HSR	high shear rate (shear rate = $10^4\ s^{-1}$)
KU	Krebs units, values of a scale used to express the consistency of paints measured by a Stormer viscometer
LSR	low shear rate (shear rate = $2\ s^{-1}$)
MCC	microcrystalline cellulose
NVV	nonvolatiles by volume
POE	polyoxyethylene [Fig. 1(b)]
PVC	pigment volume concentration, the ratio of pigment volume to binder + pigment



(a) Structure of Hydroxyethyl Cellulose



$$\mathrm{HO{-}(CH_2{-}CH_2{-}O)_n{-}H}$$

(b) Structure of Poly(oxyethylene)

Figure 1 Chemical structures of (a) hydroxyethyl cellulose (HEC) and (b) polyoxyethylene (POE).

EXPERIMENTAL

Materials

The characteristics of associative thickeners used in this study are listed in Table I. The information on latices studied are given in Table II.

Phase Separation

Samples of each composition were placed in 20 mL vials and allowed to stand undisturbed. Both latex/thickener dispersions and coating formulations were made at 32% nonvolatile by volume (NVV). Data were taken periodically over the course of 2 months. No significant changes in the volume of the upper phase changed after 2 months and these are the values reported.

Table I Characteristics of Associative Thickeners

Thickener	Supplier	M_w	M_n	M_w/M_n
HEUR-100	Cortex	10,848	8,679	1.3
HEUR-200	Union Carbide	71,400	44,600	1.6
HEUR-270	Union Carbide	74,800	49,000	1.5
HEUR-708	Rohm & Haas	37,000	23,200	1.6
NPIP $(EtO)_{595}$IPNP	NDSU	31,800	24,000	1.3
$[NP(EtO)_{100}IPDI]_3$	NDSU		10,500	

Three criteria were used to characterize the appearance of the phase-separated samples. The first was the volume fraction of the separated phase, a ratio of upper-layer volume to total volume. The second was the visual observation of the upper-phase viscosity. This was very qualitative in nature and served only to provide some insight into the thickener's presence in the upper layer. The last was the visual observation of the upper-phase appearance. This information describes the cleanness of separation between the two phases.

Coating Formulations

Coatings were made from a constant pigment grind; the general composition is given in Table III(a). The pigment dispersion was prepared in a disperser at high speed (2400 rpm) until 6.5 NS (Hegman fineness of grind test) (ASTM D 1210-79) was achieved. The grind was divided into small samples and mixed with the latex and thickener, etc., listed in Table III(b), under carefully controlled agitation.

The rheological properties were determined with a Stormer viscometer (ASTM D562-85) and cone/plate viscometers. Flow and leveling (ASTM D 4062-81), sag resistance (ASTM D 4400-84), scrub resistance (ASTM D 2486-74), and degree of blistering (ASTM D 714-87) of the applied dry films were evaluated.

RESULTS AND DISCUSSION

Studies of the phase separation behavior of a nonadsorbing model system, hydroxyethyl cellulose (HEC)-thickened poly(methyl methacrylate) (PMMA) latices,[21-23] delineate that the HEC concentration (C_f) required to flocculate the latex increases with decreasing HEC molecular weight, and with a given molecular weight, C_f decreases with increasing median particle size of the latex. HEURs have been touted as materials that can overcome some of the deficiencies described earlier for HEC-thickened coating formulations. They have gained wide acceptance, alone and in combination with cellulose ethers, in coatings formulations that contain a multitude of components. One of the undesirable consequences of HEUR use is notable syneresis[16] in some formulations. When colorants are used, phase separation detracts from an aesthetic appearance.

I. Model Thickeners/Commercial Latices Dispersions

A. Nonhydrophobe-modified Thickeners

1. Hydroxyethyl Cellulose (HEC). Control thickeners, HEC and polyoxyethylene (POE) (Fig. 1) of different molecular weights are examined to provide information on phase-separation phenomena without the complication of hydrophobes at-

Table II Characteristics of Commericial Latex

Latex	Chemical Composition	Supplier	Particle Diameter (nm)	Surface Grafted HEC[20]
AC-234	All-acrylic	Rohm & Haas	117	—
AC-417	All-acrylic	Rohm & Haas	650	Yes
AC-490	All-acrylic	Rohm & Haas	390	—
AC-64	All-acrylic	Rohm & Haas	560	—
UCAR-367	Vinyl–acrylic	Union Carbide	525	Yes
UCAR-376	Vinyl–acrylic	Union Carbide	270	Yes

Table III Paint Formulations (100 g)[a,b]

(a) Pigment Grind

Component	Supplier	Description	Weight (g)
Water	—	Dispersing medium	20.000
Tergitol 15-S-9	Union Carbide	Wetting agent	0.300
Colloid 581 B	Colloids Inc.	Antifoam	0.370
Tamol 850	Rohm & Haas	Dispersant	0.470
Ethylene glycol	Aldrich	Cosolvent	1.700
Phenyl mercuric acetate	Key Chemicals	Fungicide	0.001
TiO_2 (Tipure R-900)	DuPont	Pigment (rutile TiO_2)	21.750

(b) Let-down

	Weight (g)			
Component	AC-64	AC-417	UCAR-367	UCAR-376
Water	13.62	3.18	9.61	8.46
Latex	40.08 (60.5% NVW)	50.52 (48% NVW)	44.09 (55% NVW)	45.24 (55% NVW)
Texanol[c]	1.70	1.70	1.70	1.70
Thickeners[d]	Weight needed to achieve a given Stormer viscosity			

[a] Pigment volume concentration is 0.21.

[b] Nonvolatile by volume is 0.32.

[c] Coalescing aid.

[d] The amounts of thickeners required are given in the Tables IV–XIV.

tached to the thickener. The latices used in this part of our study were three all-acrylic binders, Rhoplex AC-234 (117 nm); AC-490 (an intermediate median-size latex, 390 nm with an intentional blend (5 wt %) of small particles for flow control); and a large binder, AC-64 (560 nm). The degree of phase separation in the 700,000 molecular weight HEC dispersions (Table IV) correlates with findings by Sperry et al.[21–23]: the larger latex exhibits phase separation. Considering that these latices contain different amounts and types of nonsurfactant stabilizers, correlation with the general VRF concept was not a given result.

The largest latex, AC-64, exhibits the highest volume fraction of the separated phase with the lowest concentration of HEC. As the HEC concentration is increased to 1.0 and 1.3 wt %, based on the aqueous phase, the volume of the separated phase decreases. This phenomenon, also observed by Sperry et al.[21–23] is explained by the increasing rigidity of flocculent structures with increasing thickener concentration. Some of the separated phase is trapped in the lower-phase layer. As the HEC concentration was increased, the viscosity and the cloudiness of the upper layer increased.

2. Polyoxyethylene (POE). Dispersions containing linear POE thickeners of three molecular weights were made at one concentration only (ca. that required to achieve a 90 KU coating viscosity). The amounts of POE are significantly greater than is the concentration of HEC used because of their lower molecular weights. The extent of syneresis with the largest latex is lower than with HEC (Table V), but it is observed with the two larger latices with all three unmodified POEs. With very large amounts of the low molecular weight POE ($M_v = 1.2 \times 10^4$), syneresis is observed with all three latices.

B. Model Hydrophobically-Modified Thickeners

The structures of model HEUR thickeners synthesized in our laboratories are given in Figure 2. The model that has been examined extensively in our studies[24] is NPIP$(EtO)_{595}$IPNP [Fig. 2(a)], which is an analog of the HEUR-708 commercial associative thickener, except our model has no internal hydrophobes. The model NPIP$(EtO)_{595}$IPNP thickener is unique in that it exhibits no visible phase-separation behavior with any of the three latices

Table IV Phase Separation of 32% NVV Commercial Acrylic Latex Dispersions Thickened with Hydroxyethyl Cellulose

			2 Months	
Latex (Medium Size)	Wt % on Aq Phase	Vol Fraction Separated Phase	Separated Phase Visual Viscosity	Separated Phase Appearance
AC-234 (117 nm)	0.7	-----	-----	-----
	1.0	-----	-----	-----
	1.3	-----	-----	-----
AC-490 (390 nm)	0.7	-----	-----	-----
	1.0	-----	-----	-----
	1.3	-----	-----	-----
AC-64 (560 nm)	0.7	0.38	Nonviscous	Mostly clear
	1.0	0.21	Intermediate viscosity	Less clear
	1.3	0.21	Viscous	Cloudy

Dashed lines indicate no visible phase separation.

(Table VI). Dispersions containing this thickener exhibit structuring and extreme shear thinning.[25] The gel-like appearance (applesauce consistency), the presence of a yield stress in the thickened solution, and the high elasticity of this thickener in the presence of other coating formulation components[26] is indicative of strong intermolecular associations. Commercial associative thickeners associate in solution free of other components, but they do not exhibit the high solution yield stress observed with the NPIP(EtO)$_{595}$IPNP thickener.

The model (NP(EtO)$_{100}$IPDI)$_3$ HEUR (Fig. 2b) with an extremely large internal hydrophobic unit, and with only a small number of oxyethylene units separating the terminal surfactant hydrophobes, exhibits extreme phase separation in aqueous solution, alone and in the presence of anionic and nonionic surfactants.[26] It is not surprising that the latex dispersions follow the phase behavior observed with this thickener (Table VI).

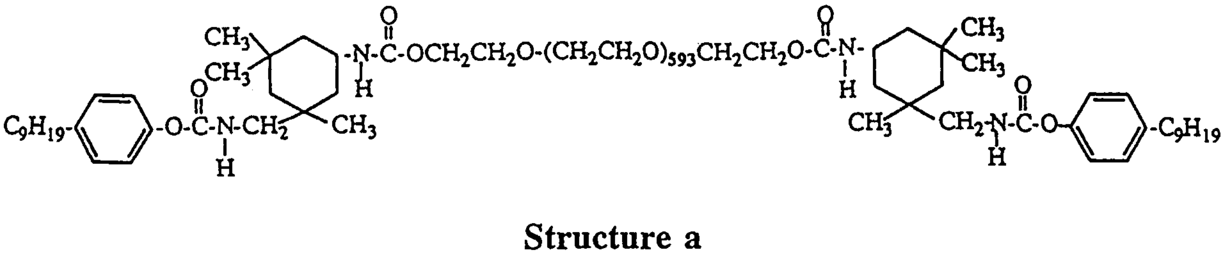
II. Commercial HEUR Thickeners/Model Latex Dispersions

A generic structure for commercial HEUR associative thickeners is given in Figure 3. The degree of

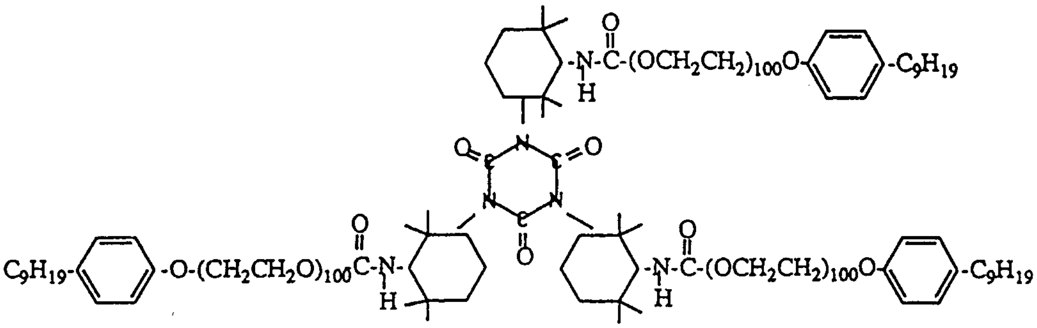
Table V Phase Separation of 32% NVV Commercial Acylic Latex Dispersions Thickened with Poly(ethylene oxide)

			2 Months	
[M_v (10^4)]	Wt % on Aq Phase	Vol Fraction Separated Phase	Separated Phase Visual Viscosity	Separated Phase Appearance
AC-234 (117 nm)				
10.0	6.5	-----	-----	
3.5	9.0	-----	-----	
1.2	11.0	0.10	Nonviscous	Separations in pockets, cloudy
AC-490 (390 nm)				
10.0	6.5	0.04	Nonviscous	Cloudy
3.5	9.0	0.08	Nonviscous	Cloudy
1.2	11.0	0.10	Nonviscous	Cloudy
AC-64 (560 nm)				
10.0	6.5	0.05	Nonviscous	Cloudy
3.5	9.0	0.08	Nonviscous	Cloudy
1.2	11.0	0.10	Nonviscous	Cloudy

Dashed lines indicate no visible phase separation.



Structure a



Structure b

Figure 2 Chemical structures of model HEUR associative thickeners.

polymerization of commercial HEURs is determined by the reaction time and by the ratio of diisocyanate to polyetherdiol. The highest M_v POE in the preceding section was approximate to the molecular weight of two commercial urethane associative thickeners HEUR-200 and -270; the 35,000 M_v POE is close to that of HEUR-708. None of the commercial HEUR thickeners would be made from either the 100,000 or 35,000 M_v POEs for statistical and manufacturing reasons. Diisocyanate coupling of lower M_v POE is the manufacturing technique used to build the molecular weight of commercial HEURs; the 1.2×10^4 M_v represents the upper limit of POE that would be used in production.

In prior studies[27] with model latices of 200 nm diameter, phase separation was observed with both HEUR-708 and -270 when the amount of surface acid segments and free surfactant was low. With increasing latex surface acid and excess surfactant, phase separation was not apparent with either HEUR thickener. Thus, if the latex is not properly stabilized, the thickener can effect phase separation via adsorption on and interbridging of dispersed particles.[27-29] In commercial latices, this is unlikely due to the excess of surfactant present and the use of grafted surface stabilizer.

III. Commercial Associative Thickeners/ Commercial Latex Dispersions

There is a synergistic viscosity in many latex/HEUR dispersions. An ion–dipole interaction between latex surface acids and the ether linkages of HEUR associative thickeners may account for some of this increased viscosity.[29] Another source of this increase is the amount of free surfactant present in the final dispersion and its interaction with the hydrophobes of the HEUR thickener. Adsorption of associative thickeners on latex surfaces resulting in an increase in the effective volume fraction of the dispersed phase is another possible contribution to the viscosity of the dispersion. There are many prior studies indicating that adsorption does not occur[30] with the more significant commercial HEUR-708. For example, in systems containing sufficient surfactant, HEUR-708 is displaced from latex surfaces.[30,31] In summary, one can no longer predict phase separation based on the size of a thickener molecule and its concentration or on the median particle size of the latex. The data in Table VII highlight the complexity in response.

The 390 nm median-size latex with 5% small (about 100 nm) latex is the only binder that phase-

Table VI Phase Separation of 32% NVV Commercial Latex Dispersions Thickened with Model HEURs

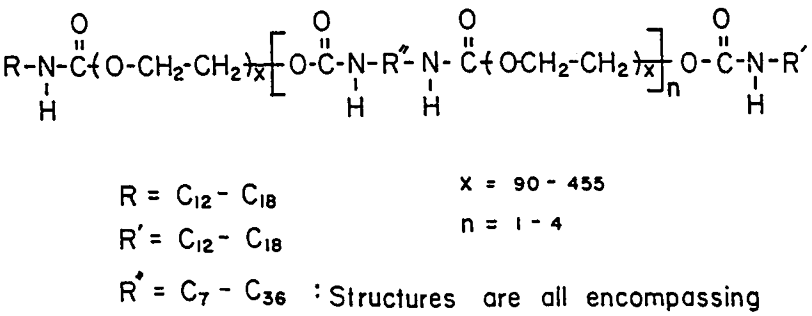
			2 Months	
Latex (Medium Size)	Wt % on Aq Phase	Vol Fraction Separated Phase	Separated Phase Visual Viscosity	Separated Phase Appearance
NPIP $(EtO)_{595}$IPNP				
117 nm	0.7	-----	-----	-----
	1.2	-----	-----	-----
390 nm	0.7	-----	-----	-----
	1.2	-----	-----	-----
560 nm	0.7	-----	-----	-----
	1.2	-----	-----	-----
$[NP(EtO)_{100}IPDI]_3$				
117 nm	1.2	Traces	Separated in pockets, cloudy	
	1.7	Traces	Separated in pockets, cloudy	
390 nm	1.2	0.18	Nonviscous	Sediment layer
	1.7	-----		Separated in pockets
560 nm	1.2	0.33	Nonviscous	In both cases, cloudy, uneven sediment layer, upper layers appears to be separating into two phases
	1.7	0.41	Nonviscous	

Dashed lines indicate no visible separation.

separated with the addition of commercial associative thickeners HEUR-270 or HEUR-100. In contrast, HEUR-200 effects phase separation of the small and larger latices, but not the intermediate size, bimodal one. HEUR-708 effects syneresis only with the 117 nm latex. The studies described in the first two sections (i.e., model thickeners [HEC, POE, and model HEURs] with commercial latices and commercial HEURs with model latices) are not broad enough to provide an adequate understanding of the data provided in Table VII. Our studies on more complex HEUR structures to expand our data base are continuing.

IV. Coating Formulations with Large Market Volume Commercial Latices Containing Commercial HEUR Thickeners

This phase of the investigation focuses on the large market volume, commercial latices in exterior (Rhoplex AC-417) and interior (UCAR-367) architectural coatings. These latices are large in particle size (> 500 nm) and, in the VRF concept, are optimum for secondary minimum flocculation. Both large latices have HEC fragments grafted to their surface, a reality not addressed in the VRF concept. Since the phase-separation response is so variant



$$\mathrm{R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}(O{-}CH_2{-}CH_2)_x{-}\left[O{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{N}{-}R''{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}(OCH_2{-}CH_2)_x\right]_n{-}O{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{N}{-}R'}$$

Figure 3 A generic structure of commercial HEUR associative thickener.

Table VII Phase Separation of 32% NVV Commericial Latex Dispersions Thickened with Commercial HEURs

			2 Months	
Thickener Latex	Wt % on Aq Phase	Vol Fraction Separated Phase	Separated Phase Visual Viscosity	Separated Phase Appearance
HEUR-270				
117 nm	0.7	-----	-----	-----
	1.7	-----	-----	-----
390 nm	0.7	0.22	Nonviscous	Clear, sediment surface uneven
	1.7	-----	-----	
560 nm	0.7	-----	-----	-----
	1.7	-----	-----	-----
HEUR-200				
117 nm	0.7	0.15	Nonviscous	Cloudy, possibly small amount of latex present
	1.2	0.27	Nonviscous	
	1.7	0.02	Nonviscous	
	2.7	-----	Pockets of separated phase	
	3.2	-----	Pockets of separated phase	
390 nm	0.7	-----	-----	-----
	1.2	-----	-----	-----
	1.7	-----	-----	-----
	2.7	-----	-----	-----
	3.2	-----	-----	-----
560 nm	0.7	0.48	Nonviscous	Cloudy, possibly small amount of latex present
	1.2	0.23	Nonviscous	
	1.7	0.10	Nonviscous	
	2.7	0.05	Nonviscous	Cloudy, possibly small amount of latex present
	3.2	Small amount		
HEUR-100				
117 nm	0.7	-----	-----	-----
	1.7	-----	-----	-----
390 nm	0.7	0.13	Nonviscous	Clear, sediment surface uneven in both cases
	1.7	0.23	Nonviscous	
560 nm	0.7	-----	-----	-----
	1.7	-----	-----	-----
HEUR-708				
117 nm	0.7	0.20	Nonviscous	Clear
	1.2	0.20	Nonviscous	Clear
	1.7	-----	-----	-----
390 nm	0.7	-----	-----	-----
	1.2	-----	-----	-----
	1.7	-----	-----	-----
560 nm	0.7	-----	-----	-----
	1.2	-----	-----	-----
	1.7	-----	-----	-----

Dashed lines indicate no visible phase separation.

Table VIII Phase Separation of HEUR-thickened Coatings[a] of Large-Particle, Large Market Volume Latices

Thickener Concn (% wt)	Stormer Viscosity (KU)	LSRV (Pa s)	Vol Fraction of Upper Layer (%)	Upper Layer Viscosity (Visual)	Upper Layer Appearance
Latex: RHOPLEX 417, 650 nm					
HEUR-270					
0.2	61	1.00	5.1	Nonviscous	Clear
0.4	92	4.01	2.4	Nonviscous	Clear
0.6	121	8.26	1.3	Nonviscous	Clear
HEUR-708					
0.2	90	2.91	2.5	Nonviscous	Clear
0.6	118	6.41	0.0	Nonviscous	Clear
Latex: UCAR 367, 525 nm, with broad particle-size distribution					
HEUR-270					
0.4	60	0.22	27.7	Nonviscous	Less clear
0.6	102	25.20	0.0	Viscous	Clear
0.6	116[b]	21.20	2.5	Viscous	Clear
HEUR-708					
0.42	89[b]	3.15	6.6	Nonviscous	Clear

[a] PVC = 0.21.

[b] A different latex manufacturing batch was used.

Table IX Phas Separations of Latex Paints[a] Thickened with HEUR and HEUR/HEC Blends

Thickener Concn (% wt)	Stormer Viscosity (KU)	LSRV (Pa s)	Vol Fraction of Upper Layer (%)	Upper Layer Viscosity (Visual)	Upper Layer Appearance
Latex: RHOPLEX 417					
270 0.3 HEC 0.1	94	4.80	3.5	Nonviscous	Clear
270 0.2 HEC 0.2	90	4.37	1.3	Nonviscous	Clear
270 0.1 HEC 0.3	87	3.97	0		
708 0.3 HEC 0.1	99	5.11	2.9	Nonviscous	Clear
708 0.1 HEC 0.3	103	6.37	0		
Latex: UCAR-367					
708 0.2 HEC 0.2	104	10.11	5.0	Nonviscous	Clear
708 0.1 HEC 0.3	107	24.77	2.6	Nonviscous	Clear
270 0.3 HEC 0.1	90	4.13	9.2	Nonviscous	Clear
270 0.2 HEC 0.2	84	3.30	11.4	Nonviscous	Clear
270 0.1 HEC 0.3	110	17.14	2.4	Nonviscous	Clear

[a] PVC = 0.21.

Table X Properties of 0.32% NVV AC-417 Latex Paints[a] Thickened with HEUR/HASE TT-935 Blends

Thickener Concn (wt %)		Stormer Viscosity (KU)	LSRV (Pa s)	HSRV (Pa s)	Vol Fraction Upper Layer (%)
270	0.4	92	4.01	0.16	2.4
270	0.3				
HASE	0.1	97	4.13	0.17	1.3
270	0.2				
HASE	0.2	102	4.21	0.17	0.0
270	0.1				
HASE	0.3	105	4.52	0.19	0.0
708	0.3				
HASE	0.1	96	3.74	0.18	2.4
708	0.1				
HASE	0.3	108	4.48	0.20	0.0

[a] PVC = 0.21.

with commercial associative thickeners, means of eliminating this problem by increasing the low shear rate (LSR) viscosity through the addition of a second thickener is pursued. In this study, another step toward reality is taken. The latices and thickeners are studied in fully formulated coatings (Table III), and the final film properties of coatings containing both commercial HEURs (708 or 270), alone and

Table XI Properties of 0.32% NVV UCAR-367 and 376 Acetate Latex Paints[a] Thickened with HEUR/HASE TT-935 Blends

Thickener Concn (wt %)		Stormer Viscosity (KU)	Vol Fraction of Upper Layer (%)	Upper Layer Viscosity (Visual)	Upper Layer Appearance
UCAR-367					
270	0.6	102	0.0		
270	0.5				
HASE	0.1	65	9.9	Viscous	Cloudy
270	0.5				
HASE	0.2	88	3.7	Viscous	Cloudy
270	0.4				
HASE	0.3	88	3.8	Viscous	Cloudy
UCAR-376					
270	0.5	88	0.0		
270	0.4				
HASE	0.1	68	10.0	Nonviscous	Cloudy
270	0.3				
HASE	0.2	68	12.2	Nonviscous	Cloudy
270	0.2				
HASE	0.3	65	12.0	Nonviscous	Cloudy

[a] PVC = 0.21.

with the secondary thickeners, are evaluated. The four LSR viscosity modifiers used are the following:

Secondary Thickener	Composition	Supplier
HEC	M_v = 700,000	Aqualon
HASE (TT-935)	Hydrophobically modified alkali-soluble emulsion	Rohm & Haas
MCC (Avicel RC-591)	Microcrystalline cellulose	FMC
Att (Attagel 50)	Attapulgite	Engelhard

A. Phase Separation and Low Shear Rate Viscosity

The coatings were formulated to target a Stormer vicosity (ASTM D562-85) of 90 KU, a common criteria among coating formulators.

When the HEUR content is sufficiently high to effect acceptable formulation viscosities (i.e., KU), the phase-separation decreases with both AC-417 and UCAR-367 latices (Table VIII).

1. HEC as Second Thickener. Our early study[32] indicated that HEUR associative thickeners provide a more desirable rheology for 100 nm latices than does HEC, but that they are not as cost effective as is HEC in formulations containing larger particle-size latices.[33] Therefore, high molecular weight HEC was added with HEUR thickeners to achieve lower HEUR thickener concentrations in AC-417 and UCAR-367 formulations. Increasing the ratio of HEC to HEUR while maintaining a constant weight percent thickener concentration decreases the amount of phase separation (Table IX). This approach does not inhibit volume restriction flocculation, which is not bad in concept, for the floc in the secondary minimum can be easily dispersed with gentle agitation. The approach does eliminate the phase separation with the all-acrylic latex that is undesirable for aesthetic reasons. This approach decreases the amount of phase separation but does not eliminate it in the formulation containing the vinyl acetate–acrylate (UCAR-367) latex.

2. HASE (TT-935) as Second Thickener. HASE (hydrophobically modified alkali-swellable emulsion) is an anionic water-soluble polymer containing surfactant hydrophobes to complement the electrostatic contributions of the neutralized acid groups to the viscosity.[34] Ideally, as the degree of neutralization approaches 100%, the viscosities of

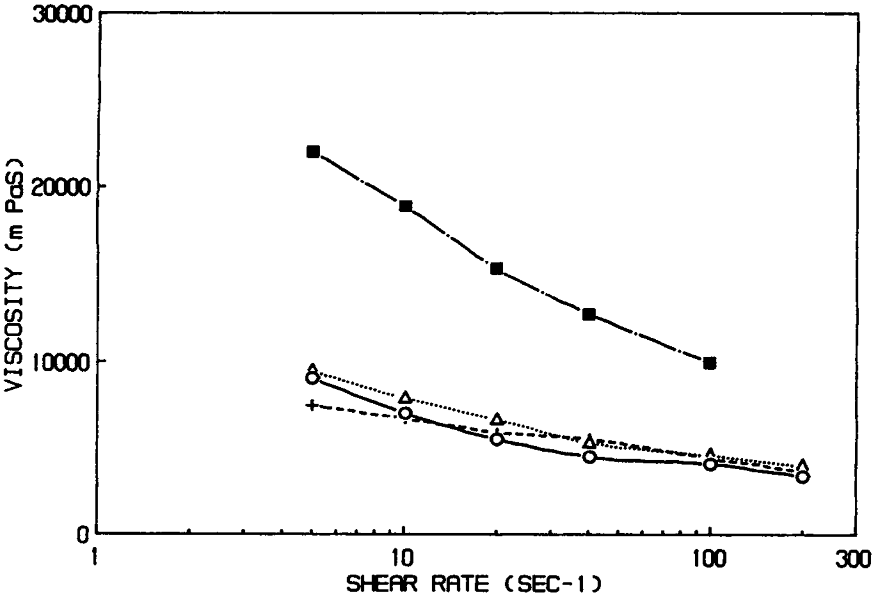


Figure 4 Viscosity vs. shear rate for UCAR-376 latex paints. Thickener concentrations are based on wt % in the aqueous phase. The HASE thickeners were not neutralized prior to addition to the paint formulations. Thickener symbols: (filled square) HEUR-270: 0.5; (cross) HEUR-270/HASE: 0.4/0.1; (triangle) HEUR-270/HASE: 0.3/0.2; (circle) HEUR-270/HASE: 0.2/0.3.

the aqueous HASE thickener dispersions reach a maximum value because of the maxima in electrostatic repulsion and effective volume fraction. It has been observed, however, that the viscosity maxima are at ionization levels less than 100% in alkali-swellable emulsions with no hydrophobes.[35,36] It has been hypothesized that the swelling should be high to allow the particles to strongly interact with each other. The unneutralized carboxyl groups at a pH 9 could more easily form intermolecular and intramolecular hydrogen bonds with other carboxyl and ester groups, leading to further viscosity enhancement. At a pH > 10, the high concentration of electrolyte reduces the electrostatic repulsions and that component's contribution to the overall viscosity.

The HASE thickener was added to the formulations as supplied (i.e., as a low pH dispersion). The coatings were then neutralized with ammonium hydroxide. According to suggested commercial formulations, pH values of final paints are adjusted to 9 for all-acrylic (AC-417) latex formulations and to about 8 for vinyl–acrylic (UCAR-367 and -376) latex formulations, because of the poor hydrolytic stability of vinyl acetate resin in alkaline media.

The AC-417 latex coating formulations thickened with HEUR/HASE combinations demonstrate both higher LSR and HSR viscosities (Table X). The values are higher than those of the corresponding formulations thickened by an equivalent amount of HEUR thickener alone. On the other hand, HASE does not viscosify UCAR-367 and UCAR-376 systems as effectively (Table XI) because of the lower dispersion pH. Moreover, the incorporation of HASE made the viscosity even lower than that of the formulation containing the same amount of HEUR thickener alone, one example being shown in Figure 4. This observation is apparently related to an undesirable interaction with the addition of NH_4OH to the full coating formulation. This has led most formulators to the preneutralization of HASE thickeners, followed by the addition of the viscous solution to the dispersion containing the other coating components.

Because of the presence of hydrophobes in HASE, some rheological behaviors are very similar to those of the HEUR thickener. As illustrated in Table X, higher viscosities at high shear rate were observed with HEUR/HASE formulations containing the large all-acrylic latex. Better flow and leveling is observed with HEUR/HASE-thickened AC-417 formulations (Table XII) than with the HEUR/HEC formulations of similar Stormer viscosities.

3. MCC as Second Thickener. Avicel RC-591 microcrystalline cellulose (MCC) is a composition of cellulose gel and sodium carboxylmethylcellulose.[37] It is not a water-soluble cellulose derivative as HEC, but a water-dispersible organic hydrocolloid. When properly dispersed in water, the individual RC-591 powder particles disintegrate and form a dispersion of cellulose microcrystal aggregates. These aggregates are elongated solid particles that range in size from a few microns to a few tenths of a micron. At concentrations greater than 1%, thixotropic gels are formed due to the linking of these

Table XII Properties of 0.32% NVV AC-417 Latex Paints Thickened with HEUR/HEC and HEUR/TT-935 Blends

Thickener Concn (wt %)		Stormer Viscosity (KU)	Leveling[a]	Sagging[b] (mil)
708	0.6	118	4	7
708 HEC	0.3 0.1	99	4	7
708 HEC	0.1 0.3	103	0	> 12
708 HASE	0.3 0.1	96	6	> 12
708 HASE	0.2 0.2	117	4	> 12
708 HASE	0.1 0.3	108	4	12
270	0.4	92	3	12
270 HEC	0.3 0.1	94	0	> 12
270 HEC	0.2 0.2	90	0	> 12
270 HEC	0.1 0.3	87	0	> 12
270 HASE	0.3 0.1	97	4	9
270 HASE	0.2 0.2	102	5	7
270 HASE	0.1 0.3	105	3	7

[a] Leveling is determined according to ASTM D 4062-81. The results are reported as the number of lines leveled (merged). Here, the maximum is 10 (best leveling), and the minimum is 0, representing poor leveling.

[b] Sag resistance is determined according to ASTM D 4400-84. Here, the maximum is > 12 mil, representing good sag resistance, and the minimum is 3 mil, representing poor sag resistance.

solid particles. The colloid-chemical behavior of Avicel RC-591 is similar to a dispersion of an expanding-lattice clay (e.g., montmorillonite). MCC as a complementary thickener does not impart viscosity to coatings when the HEUR concentrations are low (Table XIII), but raises viscosity when the HEUR concentrations are high (Figs. 5 and 6). When the MCC concentration is increased to a certain value, a yield stress is observed (Fig. 5) when the acetate latex is decreased in size (i.e., UCAR-376, but not with UCAR-367, Fig. 6); as noted with small particle all-acrylic latices, the smaller latex contributes to the dispersion's viscosity at a constant NVV.

Although MCC is ineffective in increasing the coating's viscosity, the use of a small amount of MCC (0.1–0.2% wt) can eliminate the phase separation completely for the paints having an optimized Stormer viscosity (Table XIV). The use of HEC, HASE, and clays as secondary thickeners can also minimize the phase separation, but when HEC and clays are used as secondary thickeners, poor flow and leveling is observed. The network structure of MCC does not appear to rebuild as quickly (Table XIV). This may be due to the lower density and the stronger Brownian movement of MCC particles over clay particles.[38]

4. Attapulgite (ATT) as the Second Thickener. The effort in achieving the optimized Stormer viscosity did not succeed in most of the formulations using an HEUR as the primary thickener and ATT as the secondary thickener. There appears to be a dramatic decrease in low shear rate viscosities as the formulations decrease in HEUR concentration, which prevents the comparison of their phase behaviors with other formulations. This may be related to the adsorption of the HEUR thickener on the surface of the clay and, thereby, destruction of the other interaction[26,39,40] of the HEUR thickener that contributed to the system's total viscosity.

B. Film Properties

Paints made from all-acrylic latices (AC-64 or AC-417) have much better scrub resistance (Figs. 7 and 8) than those from vinyl–acrylic latices (UCAR-367

Table XIII Properties of 0.32% NVV Latex Paints Thickened with HEUR and HEUR/MCC Blends

Thickener Concn (wt %)		Stormer Viscosity (KU)	LSRV (Pa s)	HSRV (Pa s)	Vol Fraction of Upper Layer (%)
AC-417					
270	0.4	92	4.01	0.16	2.4
270 MCC	0.3 0.1	83	3.46	0.13	2.5
270 MCC	0.2 1.3	71	4.44	0.11	0.0
270 MCC	0.1 1.5	65	3.62	0.11	0.0
UCAR-367					
270 MCC	0.3 0.1	81	4.72	0.26	17.9
270 MCC	0.2 0.2	< 53	0.84	0.25	14.6
270 MCC	0.1 0.3	< 53	0.98	0.16	19.3
708	0.42	89	3.15	0.37	6.6
708 MCC	0.2 1.4	55	1.75	0.12	32.5
708 MCC	0.1 1.8	54	5.51	0.13	18.8

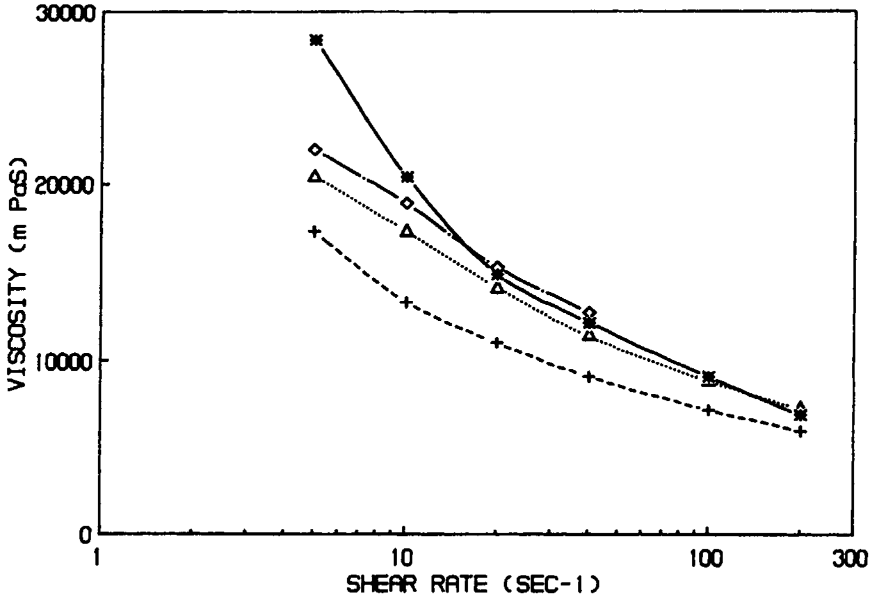


Figure 5 Viscosity vs. shear rate for UCAR-376 (a smaller particle size vinyl/acrylic binder) latex paints. Thickener concentrations are based on wt % in the aqueous phase. Thickener symbols: (diamond) HEUR-270: 0.5; (cross) HEUR-270/MCC: 0.4/0.1; (triangle) HEUR-270/MCC: 0.4/0.2; (star) HEUR-270/MCC: 0.4/0.3.

or UCAR-376). The vinyl acetate segments in UCAR-367 and UCAR-376 latices are significantly more hydroscopic and hydrolyzable than are acrylic or methacrylic segments. The influence of the latex is so dominant that the nature of thickeners is of secondary important. Results of blister test agree well with the outcome of the scrub experiment (Figs. 9 and 10). The values of scrub and blister resistances

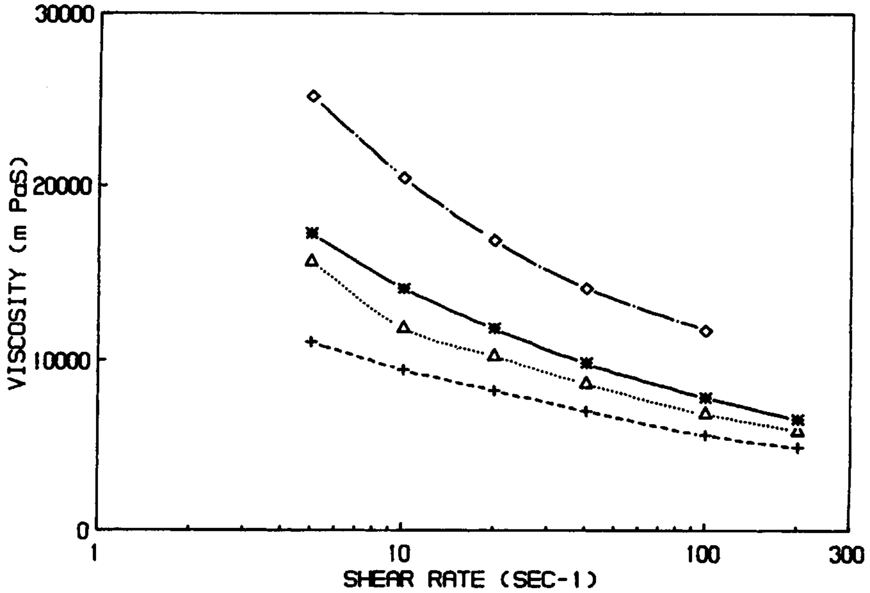


Figure 6 Viscosity vs. shear rate for UCAR-367 latex paints. Thickener concentrations are based on wt % in the aqueous phase. Thickener symbols: (diamond) HEUR-270: 0.6; (cross) HEUR-270/MCC: 0.5/0.1; (triangle) HEUR-270/MCC: 0.5/0.2; (star) HEUR-270/MCC: 0.5/0.3.

Table XIV Properties of 0.32% NVV Latex Paints Thickened with HEUR-270 and HEUR-270/MCC Blends

Thickener Conc (% wt)		Stormer Viscosity (KU)	Vol Fraction of Separation Phase (After 2 Months) (%)	Leveling	Sag Resistance
UCAR-376					
270	0.6	102	0.0		
270 MCC	0.5 0.3	92	0.0	4	> 12
270 MCC	0.5 0.2	86	0.0	5	9
270 MCC	0.5 0.1	82	0.0	5	11
UCAR-376[a]					
270	0.3	56	11.5		
270	0.4	72	7.7		
270	0.5	88	0.0		
270 MCC	0.4 0.3	89	0.0	3	8
270 MCC	0.4 0.2	85	0.0	5	9
270 MCC	0.4 0.1	77	0.0	3	8
270 MCC	0.3 0.2	65	3.8	6	5

[a] A vinyl-acrylic latex, particle diameter 270 nm.

are so low for both UCAR-367 and -376 formulations that within the experimental error the influence of different thickeners is essentially undistinguishable. These results are not surprising. The latex is the major constituent of latex paint, whereas the thickener is present in a very small quantity, though it has a large effect on the rheological properties of paint. The resistance of the dry film to deterioration by scrubbing in an aqueous soap solution would be anticipated to be inversely proportional to the amount of water-soluble material present in the film. The large amount of hydroxyl groups on HEC (Fig. 1) would impart greater water sensitivity to the film in comparison with ethoxylated HEUR thickeners. The large amount of ionized carboxyl groups at high pH makes the cross-linked HASE copolymer highly swellable and is responsible for the low scrub resistance of the corresponding paints.

The difference in the scrub resistance and the blister test between the thickeners can be observed only with the all-acrylic paints. The observed order of the scrub and blister resistance of the formulations studied were the following: MCC and ATT greater than the associative thickener alone, which is greater than HEC and HASE in combination with HEURs.

Unlike HEC, MCC is water-insoluble because of strong intra- and intermolecular hydrogen bonding. This insolubility accounts for the good scrub resistance of the corresponding paints. ATT, an insoluble inorganic material, contributes good scrub resistance in a similar manner.

CONCLUSIONS

Latex dispersions thickened with nonhydrophobe-modified thickeners exhibit greater phase separation with larger particle-size latices. This behavior was consistent with that observed previously by Sperry

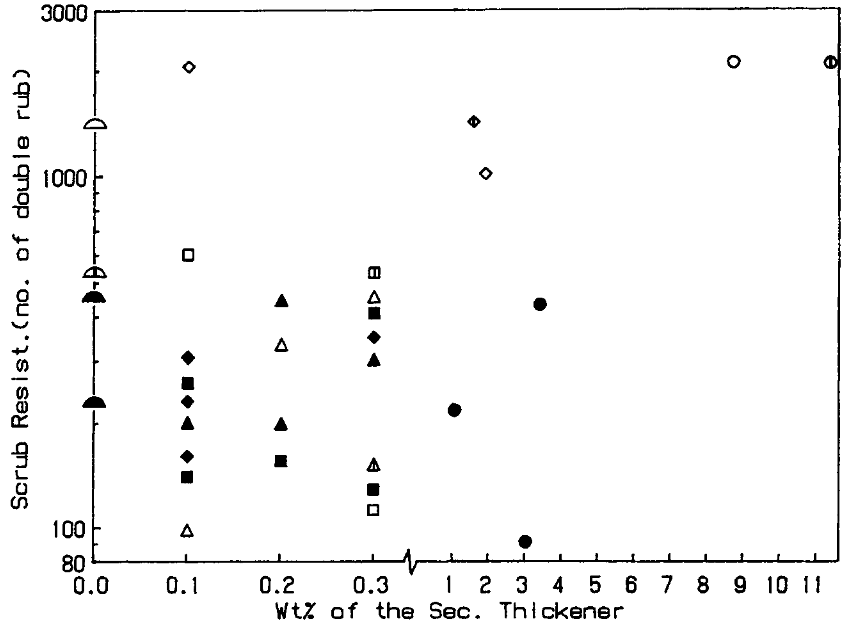


Figure 7 Scrub resistance of dried film vs. weight concentration of the second thickener in the aqueous phase. The primary thickener is HEUR-270. The concentration of the primary thickener decreases as the concentration of the second thickener increases while keeping total thickener concentration relatively constant in the formulation. Symbols for latices: (open) AC-417; (open with a vertical line) AC-64; (closed) UCAR-367. Symbols for second thickeners: (square) HEC; (triangle) TT-935; (diamond) MCC; (circle) ATT; (half-circle) HEUR-270 only, no second thickener.

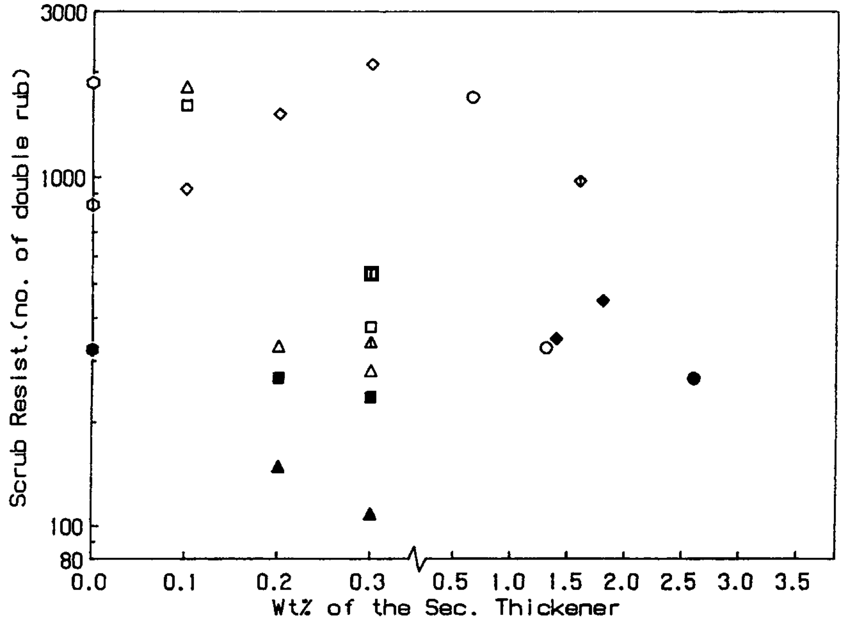


Figure 8 Scrub resistance of dried film vs. weight concentration of the second thickener in the aqueous phase. The primary thickener is HEUR-708. The concentration of the primary thickener decreases as the concentration of the second thickener increases while keeping total thickener concentration relatively constant in the formulation. Symbols for latices: (open) AC-417; (open with a vertical line) AC-64; (closed) UCAR-367. Symbols for second thickeners: (square) HEC; (triangle) TT-935; (diamond) MCC; (circle) ATT; (hexagon) HEUR-708 only, no second thickener.

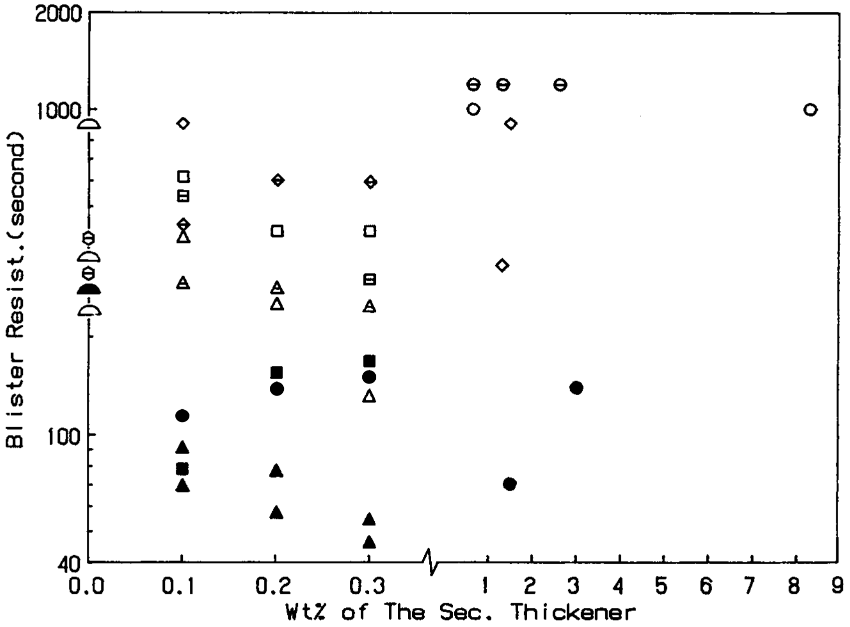


Figure 9 Blister resistance of dried film vs. weight concentration of the second thickener in the aqueous phase. Symbols for latices: (open) AC-417 with HEUR-270 as main thickener; (open with a horizontal line) AC-417 with HEUR-708 as primary thickener; (filled) UCAR-367 (the larger-size acetate latex) with HEUR-270 as primary thickener. Symbols for second thickeners: (square) HEC; (triangle) TT-935; (diamond) MCC; (circle) ATT; (half-circle) HEUR-270 only, no second thickener; (hexagon) HEUR-708 only, no second thickener.

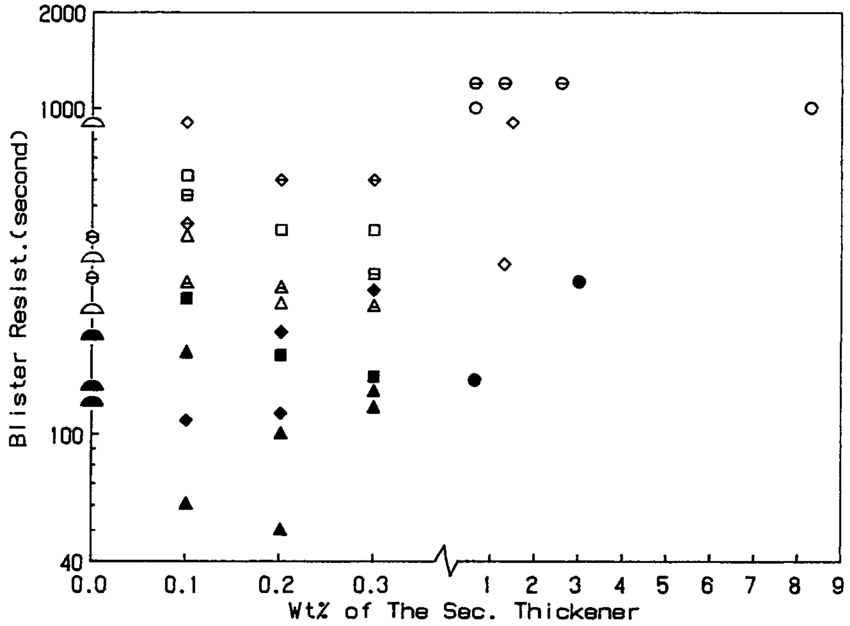


Figure 10 Blister resistance of dried film vs. weight concentration of the second thickener in aqueous phase. Symbols for latices: (open) AC-417 with HEUR-270 as main thickener; (open with a horizontal line) AC-417 with HEUR-708 as primary thickener; (filled) UCAR-376 (the smaller acetate latex) with HEUR-270 as primary thickener. Symbols for second thickeners: (square) HEC; (triangle) TT-935; (diamond) MCC; (circle) ATT; (half-circle) HEUR-270 only, no second thickener; (hexagon) HEUR-708 only, no second thickener.

et al. In latex dispersions, the presence of hydrophobes on the thickener results in various phase behaviors that are not predictable. Among model HEURs, the phase behaviors of disperse systems follow that of the HEUR thickener in the absence of a dispersed phase. A pattern was not apparent among commercial HEUR/commercial latex dispersions, and secondary thickeners imparting higher viscosity at low shear rates were used to minimize phase separation.

Hydroxylethyl cellulose as a second thickener in HEUR-thickened latex coatings decreases the amount of phase separation. HEUR and HASE thickener blends offer desired rheological properties (LSR viscosity and HSR viscosity) for all-acrylic latex paints, but reduced viscosities of vinyl–acrylic latex formulations are observed due to the formulation's lower pH.

HEUR/HEC combinations are observed to give poor flow and leveling, but good sag resistance. HEUR blends with HASE, an attapulgite (ATT) clay, or a small amount of MCC give flow and leveling properties similar to that of formulations viscosified by HEUR alone. Microcrystalline cellulose (MCC) is found to be ineffective as a secondary thickener in increasing the viscosity of latex coatings. However, the addition of a small amount of MCC (0.1–0.2% wt) to paints having optimized Stormer viscosities can eliminate the phase separation completely without affecting flow and leveling properties.

Coatings utilizing all-acrylic latex have much better scrub and blister resistance than those utilizing vinyl–acrylic binders. For all-acrylic latex paints, those thickened by MCC and ATT give the highest scrub resistance; those having a high concentration of HASE thickener give the lowest scrub value.

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