

Predicting the Water-Sensitivity of Film-Forming Coatings Additives by Water Vapor Sorption: With Application to Thickeners and Rheology Modifiers

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INTRODUCTION

An important criteria for modern day coatings is that they have good “water-resistance” or “low water-sensitivity.” This is more challenging with coatings based on waterborne and latex binders, since some of the components used to prepare the binders and those added to the finished coatings are water-soluble or water-dispersible. For architectural finishes, water-sensitivity is often defined in terms of the coating’s scrub resistance. For exterior finishes, blister resistance is important and rated in actual outdoor test fence exposures. Some of the important measures of water sensitivity for these and other coatings applications are listed in Table 1.

A formulator often has little guidance in the selection of aqueous coatings additives with regard to their potential contribution to water sensitivity. This is particularly true for rheology modifiers, thickeners, dispersants, and surfactants. If the moisture affinity of these and other components could be independently quantified, formulating for reduced water sensitivity might be facilitated by appropriate selection.

The use of paint films to quantify the water-sensitivity contribution of individual coating additives is a formidable task. This is because there are usually several additives in a given coating formulation which confound any attempt for independent examination. In addition, the possibility for variable response within different coatings matrixes exists which could be a function of additive concentration, the type and amount of other components present (including binder and pigments), interaction with those components, distribution within the coating matrix, degree of flocculation, and the additives effects on dispersion, coating hardness, and film coalescence. For these reasons, the primary objective of the work presented here was to develop a suitable method for quantifying the water-sensitivity of individual coatings additives with respect to affinity for moisture in the absence of other coating components. Further objectives were that the method should be uncomplicated, so that any coating lab, large or small, would be able to conduct the test procedure without special equipment requirements, that it have high

Although present in relatively low concentrations, additives such as thickeners, rheology modifiers, dispersants, and surfactants can contribute to the water sensitivity of coatings due to their inherent affinity for moisture. Because of the number of additives often present and the variable response possible within different formulations, a method was sought to examine the moisture affinity of individual additives in the absence of other coating components. A simple gravimetric procedure with high sensitivity and good repeatability was developed based on water vapor sorption (WVS). In this paper, the technique is applied to a variety of commercial thickeners and rheology modifiers commonly employed in waterborne coatings. Although alkali-swellaable emulsions of the conventional (ASE) and associative (HASE) varieties are generally considered to be more water sensitive than nonionic thickener types, these carboxyl functional polymers in their acid form actually showed much lower moisture affinities. WVS for the anionic ASE and HASE thickeners was a function of polymer composition, type of counter ion, base volatility, dry time, and the state of neutralization prior to conducting the test.

sensitivity, and that it have good repeatability. A final objective was to generate an initial base of water sensitivity data for a broad variety of commercial thickeners used in coatings with some rationalization of the results obtained.

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Table 1—Some Primary Measures of Water-Sensitivity by Type of Coating

Coating Type	Measure of Water-Sensitivity
Interior architectural	Scrubs, wet abrasion
Exterior architectural	Blistering, flaking, peeling
Industrial and automotive	Corrosion, blistering
Furniture coatings	Blushing, water spotting
Adhesive coatings	Adhesion, tensile properties
Barrier coatings	Vapor transmission

CONCEPTS/THEORY

Causes of Water-Sensitivity

A key fundamental assumption in the development of a method to quantify the water sensitivity of coating additives is that “the relative water sensitivity of a coating is largely a function of its ability to attract or repel moisture.” The greater a coating’s affinity for moisture, the more moisture will be absorbed into that coating, eventually resulting in some type of failure (e.g., loss of adhesion, low scrubs, blushing, corrosion, blistering, etc). To illustrate the extent to which failures may occur, extreme examples of blistering on exposure to moisture of coatings containing water-sensitive components are shown in *Figures 1 and 2* over metal and wood substrates. It is also reasonable to assume that the attraction for moisture is somewhat additive. If many of the components present are water sensitive, large amounts of water will be absorbed in a short period of time, and rapid failure is probable. If only one component is water-sensitive, it may or may not be a problem depending on the degree of water sensitivity (i.e., affinity for moisture) for that component and its concentration in the formulation. A recent theory proposed by Bassett¹ is that each coating has a “hydrophilic budget” with respect to the presence of a given water sensitive component. When the concentration of that component exceeds the budget, coating failures occur. This model is further expanded to include all of the water sensitive components within a coating where the hydrophilic budget is presumably some function of the number of hydrophilic components present, the concentrations of those components, and their respective moisture affinities. Being the primary ingredients in most coatings, the relative

hydrophilicity contribution of hydrophobic components (e.g., latex binders and some pigments) is obviously a major factor in the development of a comprehensive model.

Among the coating components which are generally considered water sensitive are surfactants, dispersants, thickeners, and rheology modifiers. Since the terms rheology modifier and thickener are often used interchangeably, particularly with respect to the associative products, they will collectively be referred to as just thickeners hereafter. Virtually all of the thickeners, most of the dispersants, and some of the surfactants used in coatings are polymeric or oligomeric film-formers. In practical applications, some of these polymeric additives are deemed to be less water sensitive than others and have fallen into favor either by promotion or based on an extensive history of testing. Paradigms also exist regarding the relative performance of polymer classes. For example, conventional wisdom suggests that nonionic polymers should be less water sensitive than anionics, and that low molecular weight materials should be more water sensitive than those of higher molecular weight. Some of these concepts will be tested in the examination of thickeners for moisture affinity by the test method developed.

Moisture Affinity Methods

A variety of methods have been applied to determine the absorption (or just sorption) of moisture into polymer films²⁻⁶ and coatings.⁷⁻¹⁸ Two practical methods commonly employed involve gravimetric determinations. The first is by the direct immersion of a coating film (free form or on a coupon substrate) of known dimensions in water. The film is then removed from the water after a fixed period of time, blotted to remove surface moisture, and subsequently weighed to determine moisture uptake. This method works reasonably well for most clear and pigmented coatings with good film integrity, but it has severe limitations for the examination of most film-forming coatings additives. For example, if the additive is a water-soluble polymer, of which many thickeners and dispersants are, the polymer will simply dissolve, and no determination of sorption can be made. Some materials also become tacky making blotting problematic and resultant weighings imprecise. A more adaptive technique and the one chosen for our work is based on water-vapor sorption (WVS)—the ab-

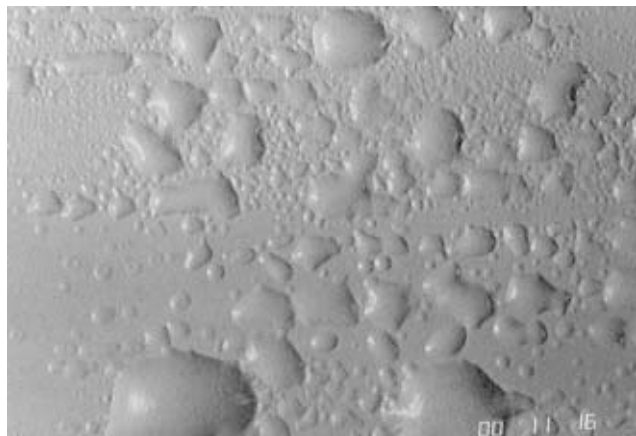


Figure 1—Severe blistering on a metal substrate upon exposure of coating to warm water vapor.

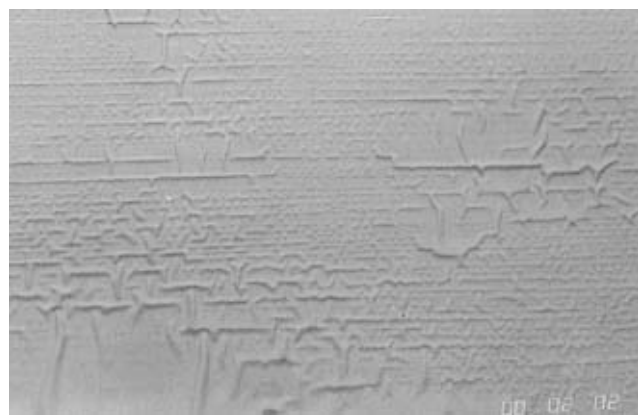


Figure 2—Severe blistering on a wood substrate on exposure of coating to overnight rain.

sorption of moisture from the gas phase with permeation into the film sample specimen. With the development of proper technique as described later, the disadvantages associated with direct immersion were avoided.

Water Vapor Sorption Theory

The mechanism of absorption of water into hydrophilic polymers was explained by Flory.¹⁹ Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions. For the purposes of our study, the substance being transported is water, and the transport is from the gaseous vapor state with absorption into a polymer film. It is well known that the sorption curve for a plane sheet (e.g., thin film) is described by a relationship between the amount of substance sorbed M_t in the specimen and the square root of time t divided by the specimen thickness b . For films following Fick's law, the sorption curve shows a linear increase in the initial stage of water uptake followed by a saturation plateau as depicted in Figure 3. From this relationship, the diffusion constant D for the polymer may be approximated.

The detailed mathematics of diffusion have been derived for a variety of geometric conditions and constraints.^{20,21} For the case of Fickian diffusion into a wide thin sheet from both sides, the mass M_t of water absorbed in time t is related to the mass absorbed at saturation M_s by equation (1).

$$\frac{M_t}{M_s} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-D(2n+1)^2 \pi^2 t / b^2} \quad (1)$$

Here it is assumed that the film thickness b is very small relative to other dimensions so that diffusion is limited to penetration through the b dimension from both sides. To arrive at this solution, the concentration of water or water vapor must be constant at the film surfaces during the diffusion process.

For exposures of short duration t , equation (1) can be replaced by the approximate following expression:

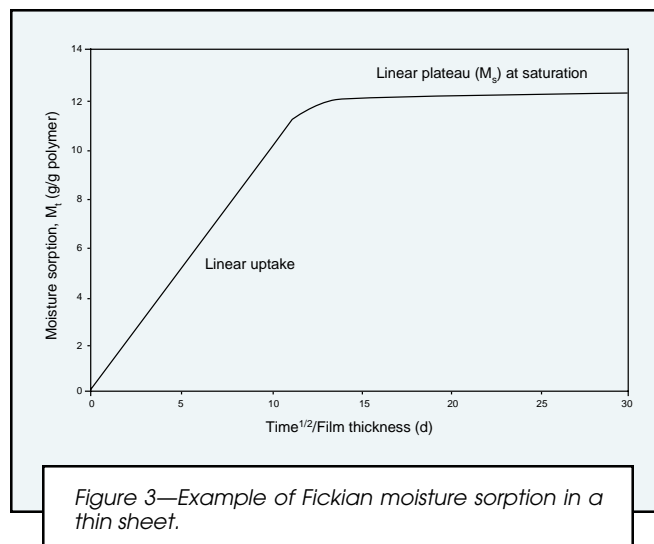
$$\frac{M_t}{M_s} = 4 \left(\frac{Dt}{b^2} \right)^{1/2} \times \left[\pi^{-1/2} + 2 \sum_{n=0}^{\infty} (-1)^n \operatorname{ierfc} \left(\frac{nb}{2\sqrt{Dt}} \right) \right] \quad (2)$$

A further approximation may be used to obtain the diffusion coefficient D with a systematic error¹⁵ of less than one percent when M_t/M_s is less than 0.6.

$$\frac{M_t}{M_s} \approx 4 \left(\frac{Dt}{\pi b^2} \right)^{1/2} \quad \text{or} \quad \frac{M_t}{M_s} \approx \frac{4}{\sqrt{\pi}} D^{1/2} \frac{t^{1/2}}{b} \quad (3)$$

Equations (1-3) define the symmetrical relationships and also apply to when there is an impermeable barrier at one film surface (i.e., when a film is coated on or otherwise is intimately in contact with an impermeable substrate such that sorption can only occur in one direction). This latter situation is used advantageously for the method development described later.

The partition coefficient K [see equation (4)] is another useful parameter which reflects the saturation level of moisture attainable for a given polymer.⁵ K is defined as the volume fraction of water contained in a unit volume of sorbed



polymer at saturation where W_s and W_d are the specimen weights at equilibrium saturation and dry, respectively, and ρ_w and ρ_p are the density of water and dry polymer, respectively.

$$K = \frac{W_s - W_d}{\rho_w} / \left(\frac{W_s - W_d}{\rho_w} + \frac{W_d}{\rho_p} \right)$$

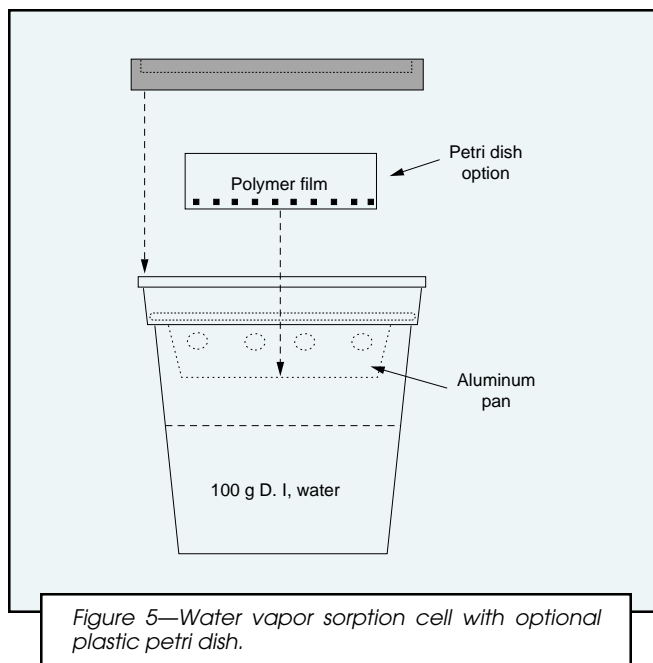
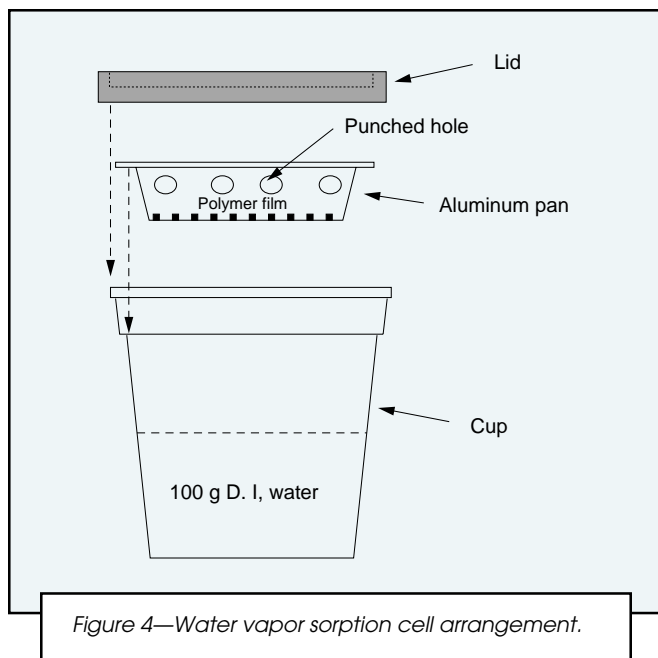
EXPERIMENTAL DETAILS

Test Method

Water vapor sorption is often conducted on rigid films and fibers of known dimensions. Although many thickeners are good film-formers at room temperature, some require cosolvents or elevated temperatures for coalescence. Still others are waxy solids on drying with distinct melting points, and others are supplied as powders that must first be hydrated for coalescence. In nearly all cases, however, continuous films of constant weight and dimensions were obtained using the tech-

Table 2—Classification of Coatings Thickeners Tested

Conventional Thickeners	
Alkali-swellable/soluble emulsions	ASE
Conventional cellulose (CC)	
Hydroxyethyl cellulose	HEC
Ethyl hydroxyethyl cellulose	EHEC
Hydroxypropyl methyl cellulose	HPMC
Sodium carboxymethyl cellulose	CMC
Synthetic biopolymers	SBP
Associative Thickeners	
Hydrophobe modified cellulose (HMC)	
Hydrophobe modified hydroxyethyl cellulose	HMHEC
Hydrophobe modified ethyl hydroxyethyl cellulose	HMEHEC
Hydrophobe Modified Nonionic Synthetics (HNS)	
Hydrophobe modified ethoxylate urethane	HEUR
Hydrophobe modified ethoxylate nonurethane	HENN
Hydrophobe modified alkali-swellable/soluble emulsion (HASE)	
Hydrophobe modified theoxylate ester ASE	HEEASE
Hydrophobe modified ethoxylate urethane ASE	HEURASE



nique described. With this procedure, the films were readily adaptable to examination by WVS with diffusion from one side through the thickness (b) dimension. Edge effect was also eliminated with an edge barrier.

To easily obtain films of uniform diameter and weight, the viscous solutions or low viscosity dispersions of the commercial thickeners being tested were simply weighed on an analytical balance into disposable aluminum pans (Fisher Cat. No. 8-732-5C), or optionally into disposable plastic petri dishes (Fisher Cat. No. 8-757-13A). Disposable plastic syringes were used for injection of the samples. Adjusting for the predetermined solids content of each thickener, the wet amount of liquid injected into each pan was computed to give a constant dry weight of polymer (e.g., 0.50 ± 0.02 g) weighed to four decimal places. With the bottom interior diameter of the dish fixed (58 mm for the aluminum pans and 52 mm for the petri dishes) and the weight of dry sample constant, the dry film thickness of each sample was also approximately constant assuming similar polymer densities. For a 0.50 g dry sample, film thickness was about 0.158 mm (6.2 mils) in the aluminum pan and 0.196 mm (7.7 mils) in the petri dishes with an assumed polymer density of 1.2 g/cm^3 .

A convection oven was used to dry each set of samples being tested to constant weight at either 50°C for four days in petri dishes or pans, or more conveniently at 95°C for 24 hr in the aluminum pans. Care was taken to place the dishes and pans on a level surface for uniform distribution and film thickness. The conditions cited for drying were necessary to obtain thoroughly dry samples and to remove any organic solvent which is commonly present in the nonionic synthetic associative thickeners. Except for the some cellulosic thickeners at the higher drying temperature, little or no degradation of the samples was apparent under the conditions cited. Only the aluminum pans could be used at the higher drying temperature due to deformation of the petri dishes above 50°C .

After drying, the samples were weighed immediately and each placed into separate humidity cells consisting of an impermeable polypropylene cup and mated polyethylene snap cap (Fisher brand, multi-purpose containers, disposable 8 oz,

cat. no. 11-840G). In the bottom of each container was placed 100 ml of deionized water. With this particular container and the specified aluminum dish, a neat fit was obtained with the rim of the dish resting on a ridge within the cup approximately 12 mm above the water line (see cell arrangements, Figure 4). To facilitate transfer of water vapor to the specimen film, eight holes measuring 7 mm in diameter were punched around the upper perimeter of each dish prior to any weighings. When in place, the container lids provided tight seals, and due to the compact vapor space dimensions, the cells became rapidly saturated with water vapor to effectively provide 100% relative humidity. To obtain accurate weighings on removal of the aluminum pans from the cells, the undersides were inspected for accumulation of any condensation and blotted dry. At no time did condensation appear on interior pan surfaces.



Figure 6—Photo of open sorption cell with aluminum pan.

When the optional petri dish was used for the sample (cell arrangement, *Figure 5*), a punched aluminum pan was first placed into the cell merely as a support for the petri dish and to permit vapor diffusion to the sample (see photographic view of open cell and support in *Figure 6*). The advantage of this latter arrangement is that condensation did not collect on the underside of the petri dishes as it occasionally did with the aluminum pans, and weighings could be made without blotting.

To obtain moisture sorption isotherms, the aluminum pans or petri dishes were periodically removed from the cells and weighed (typically at one day, three days, seven days, two weeks, and one month). Moisture sorption at time t is defined as the weight of water taken up per unit weight of dry polymer. This is often expressed as the grams water taken up (sorbed) per gram of dry polymer or simply as a percentage which is used hereafter [see equation (5)].

$$M_t = (\text{g water uptake at time } t / \text{g dry polymer}) \times 100\% \quad (5)$$

For routine determinations and product comparisons, a single point measurement at either one day, three days, or seven days was more convenient and sufficient for characterization in the initial phase of water uptake prior to saturation.

Materials

The additives tested in this evaluation were commercial thickeners and rheology modifiers from a wide range of conventional (nonassociative) and associative varieties.²²⁻²⁷ Conventional products included alkali-swellable emulsions, cellulosic polymers, and synthetic biopolymers. The associative products included one or more representative products from each major class and subclass within the classification scheme²⁸ shown in *Table 2*. The actual products tested are compiled in *Tables 3a* and *b*.

With few exceptions, all thickeners were tested as supplied including the alkali-swellable emulsions. Although the alkali-swellable emulsions of the conventional (ASE) and associative (HASE) products must be neutralized in actual practice to be used as thickeners, they were initially tested in the unneutralized state on the widely held assumption that volatile bases commonly used for neutralization leave the film on drying²⁹—this assumption is later examined for validity. The unneutralized form typically at 25-30% solids was also necessitated in many cases to obtain sufficient film weight for testing. When neutralized, most of these polymers are extremely viscous, and only samples of low solids content can conveniently be prepared which did not permit sufficient film thickness for sorption testing. For powdered samples such as the cellulose and synthetic biopolymers, adequate film formation was obtained by prehydrating the samples in the aluminum pans or petri dishes with the addition of 8 g water for 24 hr prior to drying. Solids content for samples as supplied or diluted were obtained using standard microwave or convection oven gravimetric procedures.

RESULTS AND DISCUSSION

General Observations

Three thickeners from different classifications (HASE—UCAR® Polyphobe® 9823; HEUR—Acrysol® RM-825; and

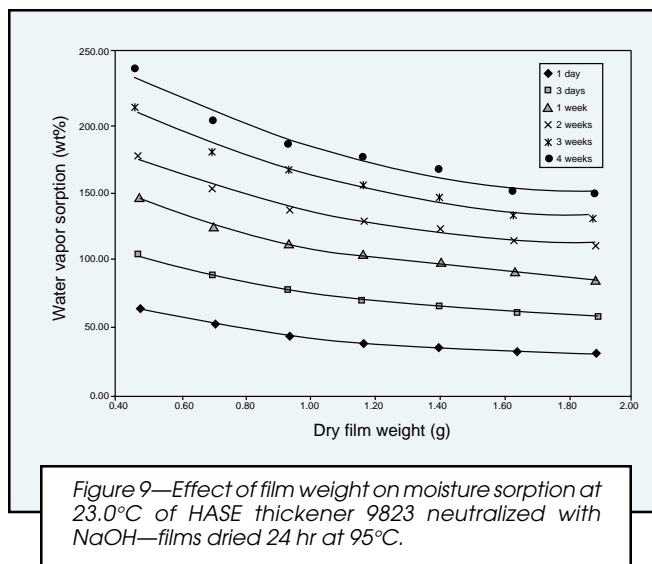
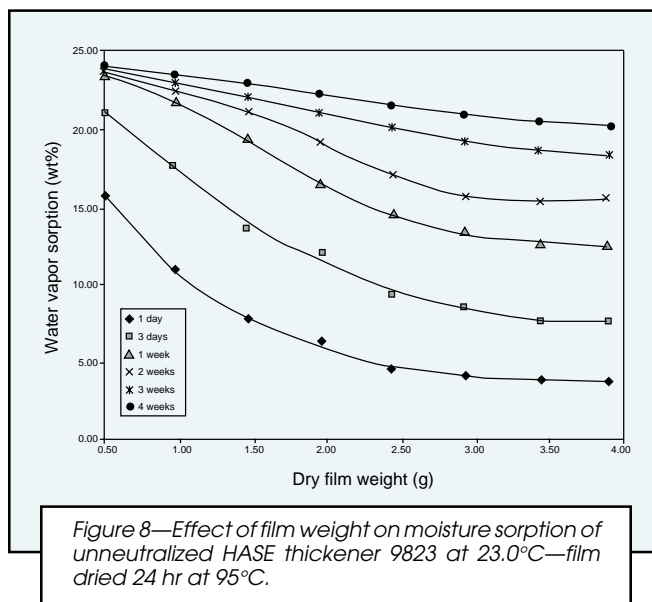
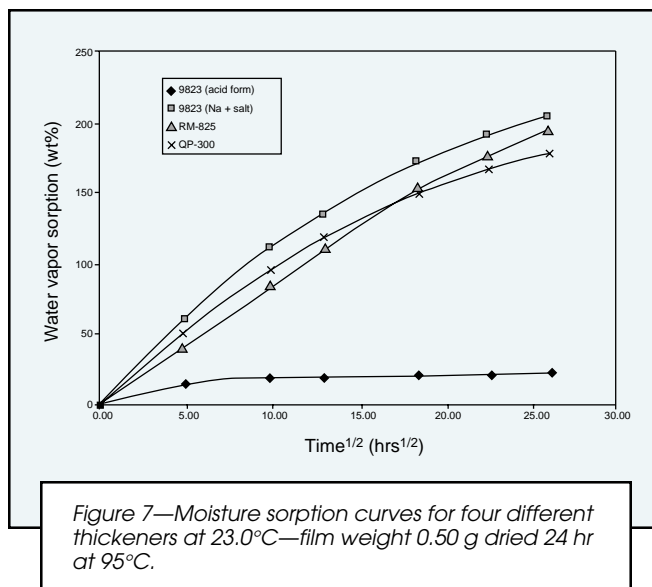


Table 3a—Thickeners Evaluated for Water Vapor Sorption

Supplier Code ^a	Tradename	Product Code	Class	Subclass
11	UCAR Thickener	146	ASE	—
10	Acrysol	ASE-60	ASE	—
10	Acrysol	ASE-108	ASE	—
1	Viscolex	HV-30	ASE	—
3	Bermocoll	E351	CC	EHEC
3	Bermocoll	E481	CC	EHEC
2	Natrosol	250 MBR	CC	HEC
2	Natrosol	250 HBR	CC	HEC
11	Cellosize	QP300	CC	HEC
11	Cellosize	ER 4400	CC	HEC
11	Cellosize	ER 52M	CC	HEC
11	Cellosize	QP100MH	CC	HEC
5	Methocel	J5MS	CC	HPMC
5	Methocel	J75	CC	HPMC
2	CMC-T	7MT	CC	CMC
2	CMC-T	7M31T	CC	CMC
7	—	K1A112	CC	SBP-RG ^b
7	—	K1A96	CC	SBP-WG ^b
7	Kelzan	XG ^b	CC	SBP-Xg ^b
9	Rheolate	1	HASE	HEEASE
1	Rheovis	CR	HASE	HEEASE
1	Rheovis	CR3	HASE	HEEASE
1	Rheovis	CRX	HASE	HEEASE
8	Alcogum	PT-33	HASE	HEEASE
10	Acrysol	RM-5	HASE	HEEASE
10	Acrysol	RM-6	HASE	HEEASE
10	Acrysol	TT-615	HASE	HEEASE
10	Acrysol	TT-935	HASE	HEEASE
10	Acrysol	TT-950	HASE	HEEASE
11	UCAR Polyphobe	101	HASE	HEURASE
11	UCAR Polyphobe	102	HASE	HEURASE
11	UCAR Polyphobe	103	HASE	HEURASE

(a) See Appendix.

(b) RG = Rhamsam gum, WG = Whelan gum, XG = Xanthan gum.

HEC—Cellosize QP-300) were chosen to examine the efficacy of the WVS test method. Because of its exceptional film forming characteristics and relatively low viscosity on neutralization, the HASE polymer in both unneutralized (acid form) and neutralized (Na⁺ salt form) was selected to determine variability in WVS due to the effects of film weight and temperature. For each of these studies, triplicate samples of polymer were dried in aluminum pans for 24 hr at 90°C. The WVS cells were placed in a controlled temperature chamber with sorption determinations made periodically over a period of up to four weeks. In the thickener comparison study, dry film weight was constant at 0.50 g with WVS conducted at 23.0°C (see Figure 7). In the film weight study, dry film weights were varied from 0.50 to 4.0 g with WVS conducted at a constant temperature of 23.0°C (see Figures 8 and 9). In the temperature study, dry film weight was held constant at 0.50 g with temperature varied for WVS from 10.0 to 40.0°C (see Figure 10).

On preliminary examination, several initial observations were made: (1) moisture sorption as a function of time in the humidity cells showed significant measurable response with good repeatability obtained in as little as one day; (2) differential response between thickener types was readily observed; and (3) only one sample (unneutralized HASE) had reached equilibrium sorption at one month, and the sorption curve obtained for this sample was similar to what would be predicted for Fickian diffusion. The results obtained also sug-

Table 3b—Thickeners Evaluated for Water Vapor Sorption

Supplier Code ^a	Tradename	Product Code	Thickener Class	Thickener Subclass
11	UCAR Polyphobe	104	HASE	HEURASE
11	UCAR Polyphobe	107	HASE	HEURASE
11	UCAR Polyphobe	114	HASE	HEURASE
11	UCAR Polyphobe	9823	HASE	HEURASE
11	UCAR Polyphobe	106HE	HASE	HEURASE
4	RHEO	2000	HASE	HEURASE
4	RHEO	2100	HASE	HEURASE
4	RHEO	3000	HASE	HEURASE
9	Rheolate	255	HMN	HEUR
9	Rheolate	278	HMN	HEUR
4	—	BR-100	HMN	HEUR
6	—	DSX-1514	HMN	HEUR
6	—	DSX-1550	HMN	HEUR
3	Bermodol	PUR 2100	HMN	HEUR
3	Bermodol	PUR 2130	HMN	HEUR
10	Acrysol	RM-1020	HMN	HEUR
10	Acrysol	RM-2020	HMN	HEUR
10	Acrysol	RM-8	HMN	HEUR
10	Acrysol	RM-825	HMN	HEUR
10	Acrysol	RM-830	HMN	HEUR
10	Acrysol	RM-870	HMN	HEUR
10	Acrysol	SCT-200	HMN	HEUR
10	Acrysol	SCT-275	HMN	HEUR
9	Rheolate	300	HMN	HENN
9	Rheolate	350	HMN	HENN
6	—	DSC 2000	HMN	HENN
3	Bermocoll	EHM100	HMC	HMHEC
2	Natrosol	FPS PLUS 330	HMC	HMHEC
2	Natrosol	FPF PLUS 430	HMC	HMHEC
2	Natrosol	PLUS 330	HMC	HMHEC
2	Natrosol	PLUS 430	HMC	HMHEC
11	Cellosize	SG-100	HMC	HMHEC

(a) See Appendix.

gested that testing at a fixed period (e.g., one day, three days, or one week) would be feasible for more convenient single-time-frame determinations.

Test Repeatability

The repeatability of the WVS test method using triplicate samples for the four previous polymers is shown in Table 4 for exposure times of one day, one week, and one month. Although the spread on triplicate samples is considered small, <5% standard deviation (SD) at all exposures, it appears that % SD increases with increasing exposure time. The % SD on other thickeners gave similar results, and testing the same polymer on different occasions also showed variability of <5% SD when a constant temperature chamber was used.

Effect of Film Weight

As predicted by diffusion theory (Figures 8 and 9), water vapor sorption values (M_t) at any time t were inversely related to film thickness (b). At $M_t < M_\infty$, thin films absorbed a higher percentage of moisture at any time t because there is less polymer absorbing a similar amount of water (i.e., the denominator is less in $M_t = \text{g water/g polymer}$). Even though the HASE Na⁺ salt absorbed much greater quantities of moisture than its acid form, both showed an approximate doubling of WVS at one day with a reduction in film weight from 2.0 g to

Table 4—Repeatability of WVS Test Results for Triplicate Samples

Thickener		WVS 1 Day	WVS 1 Week	WVS 1 Month
HASE 9823 (acid)	Ave (%)	13.9	18.7	19.2
	SD	0.4	0.9	0.8
	% SD	2.7	5.1	4.2
HASE 9823 (Na+ salt) .	Ave (%)	61.6	135.1	201.9
	SD	2.0	5.9	12.0
	% SD	3.2	4.4	5.9
HEUR 825	Ave (%)	38.6	110.9	191.3
	SD	0.6	2.7	7.8
	% SD	1.6	2.4	4.1
CC QP-300	Ave (%)	49.9	117.0	175.9
	SD	1.7	2.8	7.6
	% SD	3.5	2.4	4.3
Average	% SD	2.8	3.6	4.6

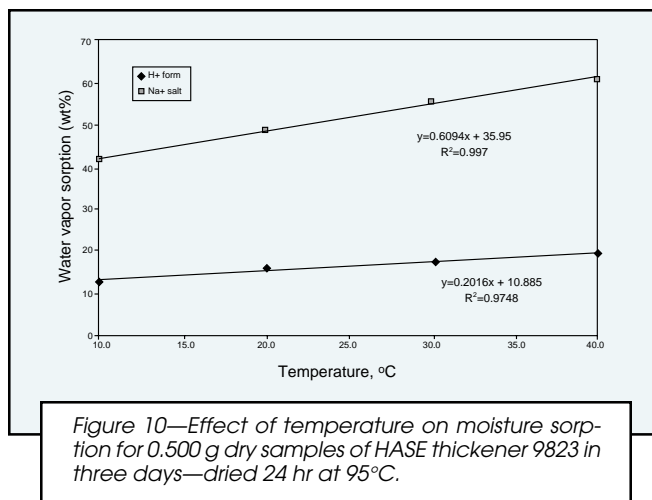
1.0 g. At one week the change in WVS for both was still similar, but the increase in WVS with the same weight reduction was less (about 50%). The results obtained suggested that maximum precision and accuracy would be obtained if dry film weights were held relatively constant when repeating a test or when comparing different products. Fortunately, control of film weight with variation of less than 10% was easily achievable in these and later WVS determinations facilitated by two factors: solids content of samples was readily determined with accuracy using conventional procedures, and wet sample weighings into the WVS pans of ± 0.05 g were also easily obtainable. For samples with high-solids contents of about 50%, variation in M_t of about $\pm 5\%$ was realized. If diluted, these and samples of lower supplied solids permitted even less variation in M_t .

Effect of Temperature

Although more difficult to obtain film uniformity, thinner films were considered desirable since they attained saturation equilibrium more quickly. A low film weight was also necessary for thickeners supplied at or diluted to low solids content (i.e., the maximum wet sample accommodated in the aluminum pans was about 20 g with holes punched, which limited the dry film weight possible). On visual inspection, the lowest film weight providing uniform and complete coverage of the pan surface for most samples was about 0.5 g dry (approximate film thickness of 0.16 mm or 6.2 mils). This weight was selected for determining the effect of temperature on WVS using HASE (UCAR Polyphobe 9823) thickener at 10% solids content.

In this study samples were dried as before, but single point WVS determinations were made at three days only. Figure 10 shows that sorption was a linear function of temperature for both the acid form and Na⁺ salt form of the HASE rheology modifier tested. The higher sorption obtained with increasing temperature was primarily due to an increase in vapor pressure which can be computed from the well-known Clausius-Clapeyron equation where P is the vapor pressure of the liquid (water in this case) and ΔH_{vap} is the enthalpy of vaporization at temperature T [see equation (6)].

$$\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + \text{constant} \quad (6)$$



From the results obtained, it was concluded that the WVS test ideally should be conducted at constant temperature. Because the temperature effect was not large, however, reasonably good results might be expected in an open lab at ambient temperature. Support for this conclusion comes from the equations derived for sorption versus temperature in Figure 10, where a variation in room temperature of $23 \pm 3^\circ\text{C}$ would produce an error in sorption of only $\pm 3.6\%$.

Comparative WVS Thickener Evaluations

On preliminary examination of other thickeners at 0.5 g dry film weight, some gave excellent substrate coverage (par-

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Table 5—Bases Used to Prepare 10 wt% Aqueous Solutions of HEURASE 9822 Thickener at pH 8.0

Neutralizing Base	Figure Designation	Base Strength	Base Volatility	Equivalent Weight	% of Theor. Base Used for pH 8.00
Ammonium hydroxide	NH ₄ OH	weak	yes	35.0	126
Sodium hydroxide	NaOH	strong	no	40.0	101
Potassium hydroxide	KOH	strong	no	56.1	97
Ammonium carbonate	(NH ₄) ₂ CO ₃	weak	yes	48.0	348
Sodium carbonate	Na ₂ CO ₃	weak	no	53.0	126
Potassium carbonate	K ₂ CO ₃	weak	no	69.1	147
2-Amino-2-methyl-1-propanol	AMP	weak	yes	89.1	104
Tris(hydroxymethyl)aminomethane	Tris Amino	weak	yes	121.1	129
Tetraethyl ammonium hydroxide	TEAH	strong	yes	147.0	100

ticularly HASE types), while others did not. Variations in film formation, surface tension, substrate wetting, and film shrinkage on drying may have been factors. Because of this, a higher dry film weight of 1.3 g was chosen for a more comprehensive thickener evaluation where complete coverage was obtained for nearly all samples tested. After drying in petri dishes to a precomputed film weight of 1.3 g for four days at 60°C, sorption determinations on approximately 64 different thickeners were conducted over a period of 28 days using the previously described cell arrangement. WVS results for the thickeners tested are compiled in Figures 11-13. At this film weight, the film thickness for samples was computed to be approximately 0.41 mm (16 mils) with an assumed polymer density of 1.2 g/cm³. Experimental results for WVS on most of the thickeners tested showed linear or near linear increases for M_t as a function of $t^{1/2}$ which is characteristic of Fickian diffusion in the linear region prior to saturation. At this film weight, however, none of the samples reached equilibrium saturation M_s in the 28-day time interval.

With both associative and nonassociative thickeners included, a most interesting result was obtained on grouping the thickeners tested into five primary classifications where data for all members in each class were averaged together (Figure 14). In their unneutralized state as tested, the alkali-swellaible thickeners (ASE and HASE) absorbed much less moisture than did the cellulosics (CC and HMC) or nonionics (HEUR and HENN) thickeners. The order for increasing sorption at later times t was ASE < HASE << HNS < CC HMHEC. The ASE and HASE polymers also appear to be approaching equilibrium in two weeks at M_t about 20%. This suggests that the commonly held notion "that alkali-swellaible thickeners are more sensitive than nonionics" is not valid at low degrees of ionization. Important assumptions are that a volatile base is used for the neutralization of the ASE or HASE polymer, and that some or all of the base leaves the film on drying before the time frame of water sensitivity assessment.

The aforementioned finding would seem reasonable when one considers the physical nature of the polymers. All of the nonionic thickeners tested, including the cellulosic and synthetic species, were water-soluble polymers as supplied. Since they are chemically unchanged when incorporated into a coating, they remain water-soluble or sensitive after the paint film has dried even though the polymer is now within an insoluble binder/pigment matrix. The ASE and HASE thickeners, on the other hand, are the only polymers tested which are made by emulsion polymerization. To produce a stable latex by this process, the polymers formed must, by definition,

be water-insoluble. Otherwise, the polymer particles formed would simply dissolve. Only on neutralization with a suitable base do the ASE and HASE polymers become water-soluble and function as thickeners or rheology modifiers. If the base used is volatile (e.g., ammonia or aminomethyl propanol, etc.), it eventually leaves the film, and the ASE and HASE polymers theoretically revert back to their insoluble form, and hence, should impart less water sensitivity (see Figure 15). If a nonvolatile base is used (e.g., KOH, NaOH, Na₂CO₃, etc.) quite a different result would be expected (high moisture affinity) and was obtained previously when WVS was conducted on the Na⁺ salt of a HASE polymer compared with its unneutralized latex form.

Effect of Neutralizing Agents with ASE/HASE

It is a generally accepted opinion of coating formulators that volatile bases eventually leave a paint film on drying. Formulating literature suggests that ammonia leaves a latex based coating in only about one day, and less volatile aminoalcohols may take up to a week. This occurs even though the latex binder, and any ASE or HASE thickeners present contain carboxyl groups, which are neutralized by the base to form ammonium polymer salts. Since the neutralization is that of a weak base with a weak acid, the state of ionization is tenuous, and equilibrium is easily shifted by volatilization of the base.

To demonstrate the loss of ammonia from a highly carboxylated thickener, FTIR spectra were obtained on a film of an ammonium hydroxide neutralized HASE polymer (UCAR Polyphobe 107) deposited on a zinc selenide ATR crystal. A 0.0027 mm film was deposited from a 0.75% aqueous solution of the thickener at pH 9.0. On drying at room temperature with periodic examination by FTIR, the disappearance of carboxyl salt (wavenumber 1550) and simultaneous appearance of free carboxyl (wavenumber 1700) was readily apparent as shown in Figure 16. Complete loss of ammonia was evident in less than 24 hr.

As discussed previously, all ASE and HASE thickeners were first examined by WVS in their unneutralized latex form. The untested assumption was that if a volatile base were used for the neutralization, the solubilized polymer would become insoluble again on evaporation of base and should then have a similar moisture affinity. If observed, any slight difference in WVS would most likely be attributable to differences in film formation, from a latex in the former case and from true solution in the latter.

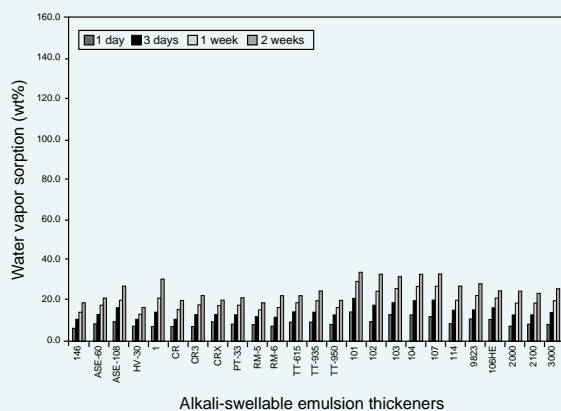


Figure 11—Moisture sorption at 23.0°C for conventional (ASE) and associative (HASE) alkali-swellable emulsion thickeners—1.30 g, dried 24 hr at 95°C.

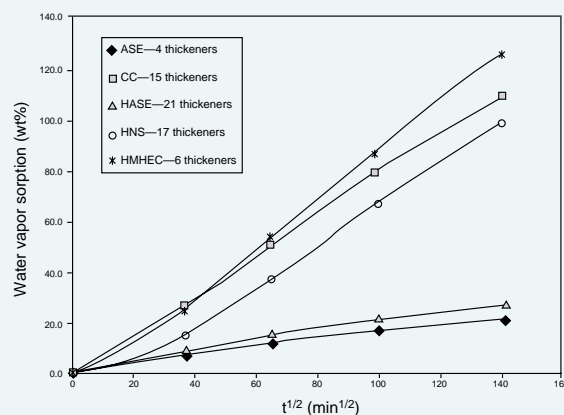


Figure 14—Composition moisture sorption curves at 23.0°C for five major classes of thickeners—1.30 g, dried 24 hr at 95°C.

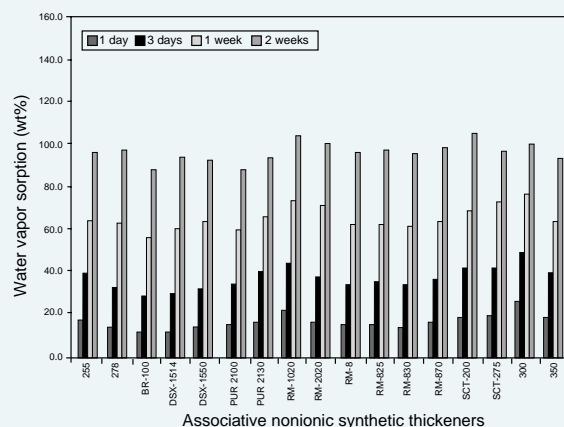


Figure 12—Moisture sorption at 23.0°C for hydrophobe modified nonionic synthetic thickeners (HNS)—1.30 g, dried 24 hr at 95°C.

Nonionic thickeners (HEC, HMHEC, HEUR)

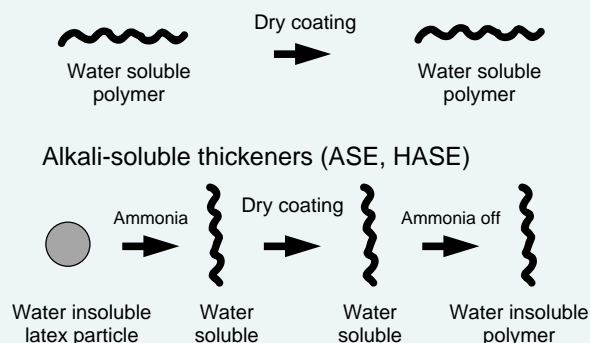


Figure 15—Theoretical water sensitivity comparison of nonionic thickeners with anionic alkali-swellable emulsion thickeners in a coating before and after drying.

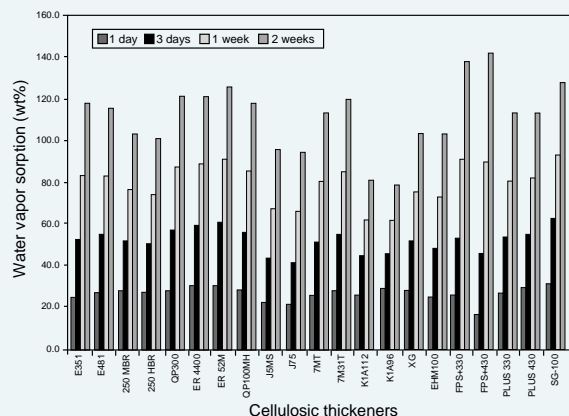


Figure 13—Moisture sorption at 23.0°C for conventional (CC) and associative (HMC) cellulosic thickeners—1.30 g, dried 24 hr at 95°C.

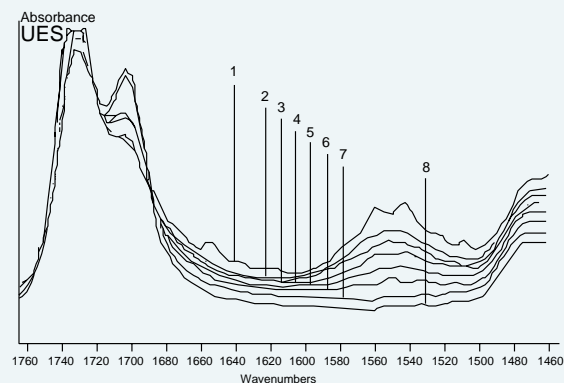


Figure 16—FTIR spectra for volatilization of ammonia from film of thickener 107 at 23°C (1 = 10 min, 2 = 20 min, 3 = 45 min, 4 = 1.5 hr, 5 = 4 hr, 6 = 12 hr, 7 = 24 hr, 8 = 1 week).

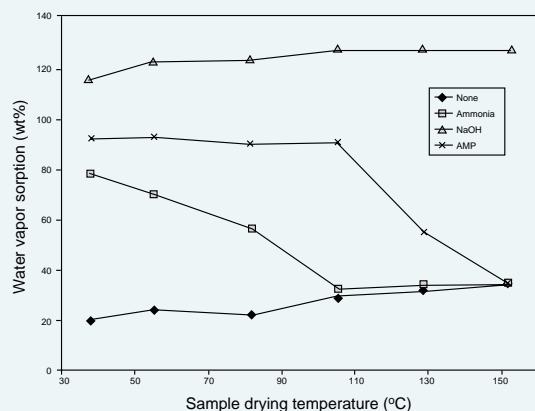


Figure 17—Effect of neutralizing agent and film drying temperature on moisture sorption of HASE thickener 9823 at 23.0°C—film weight 0.50 g dried for 24 hr at six different temperatures.

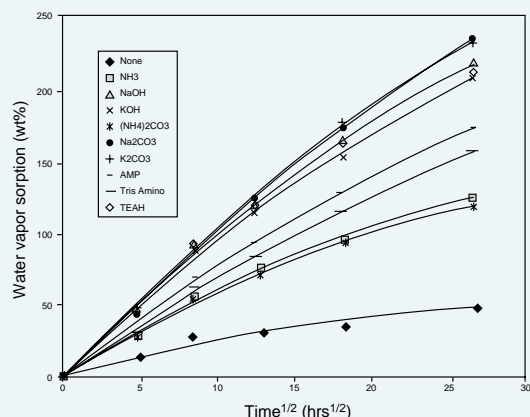


Figure 18—Moisture sorption curves at 23.0°C for various bases used to neutralize 10% aqueous solution of HASE thickener 9823 to pH 8.0—dry film weight 0.50 g dried 24 hr at 60°C with partial elimination of volatile bases.

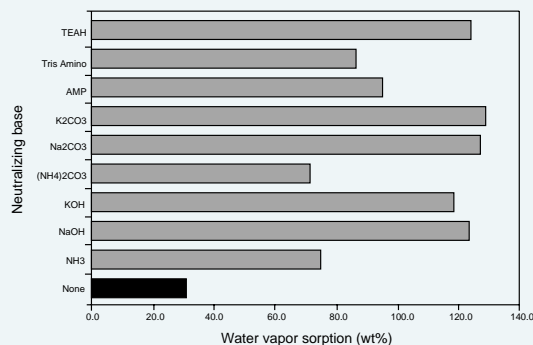


Figure 19—Effect of neutralizing bases on moisture sorption of thickener 9823 for one week at 23.0°C—dry film weight 0.50 g dried 24 hr at 60°C with partial elimination of volatile bases.

So far, it has been demonstrated by FTIR that ammonia leaves the film of a HASE polymer under ambient conditions. What is left untested is a prediction that WVS on a film from neutralized HASE polymer should be similar to that of the film cast from the same unneutralized HASE latex after a volatile base leaves the film. To examine this notion, films of ammonia neutralized HASE polymer were dried at successively elevated temperatures to accelerate liberation of the base. HASE films neutralized with 2-amino-2-methyl-1-propanol (AMP) and NaOH were also examined under the same conditions along with an unneutralized polymer control. The results of WVA conducted on the samples are shown in Figure 17. Liberation of ammonia and AMP base in this figure is suggested by the gradual reduction in M_n , and as predicted, the WVS is the same as the unneutralized polymer when all base apparently has been eliminated. The polymer neutralized with NaOH, on the other hand, retains the Na^+ ion regardless of drying conditions, and WVS remains high and relatively constant.

In one additional study, a variety of neutralizing bases shown in Table 5 were used to prepare aqueous solutions of the HASE (UCAR Polyprobe 9823) polymer at pH 8.0. WVS was then conducted on 0.50 g cast from these solutions (see Figures 18 and 19) using drying conditions of four days at 60°C which only partially removed volatile base where present. All samples containing sodium or potassium ion showed similar high WVS values, while the ammonia and amine neutralized samples were lower to varying degrees as expected.

Degree of Neutralization with ASE/HASE

From Figures 18 and 19, it is apparent that WVS is some function of the amount of base left in the HASE thickener film on drying. To examine this more thoroughly, 10% aqueous dispersions (pH < 6) and solutions (pH > 6) of the HASE (UCAR Polyprobe 9823) polymer used previously were prepared at increasing degrees of neutralization from 0 to 120% with NaOH base. The relationship obtained for pH as a function of theoretical % neutralization is shown in Figure 20. Since the Na^+ cation is not volatile, WVS determinations were expected to be some function of the carboxyl salt concentration. Figure 21 shows a positive, approximately linear, relationship between the degree of neutralization and moisture sorption. Even beyond 100% neutralization, the Na^+ ion appears to increase the affinity for moisture. Figure 22 shows the effect on WVS for films cast from these same aqueous dispersions and solutions as a function of pH. WVS rises rapidly between pH 6 and 7.

Estimation of Diffusion and Partition Coefficients

As mentioned, none of the 64 thickeners tested at the 1.3 g dry film weight reached saturation sorption M_s during the 28-day test period. Since most of the polymers examined were highly water soluble, a conclusion that sorption to infinite dilution was more likely than sorption to finite saturation seems reasonable. However, this did not appear to be the case for ASE/HASE polymers in unneutralized form. At the lower film weight of 0.5 g, one of the four polymers tested earlier (HASE—UCAR Polyprobe 9823) did reach equilibrium saturation in only a few days. Using equation (3) and the data obtained in Figure 23, it was possible to compute the approximate diffusion coefficient D for this relatively water-insoluble

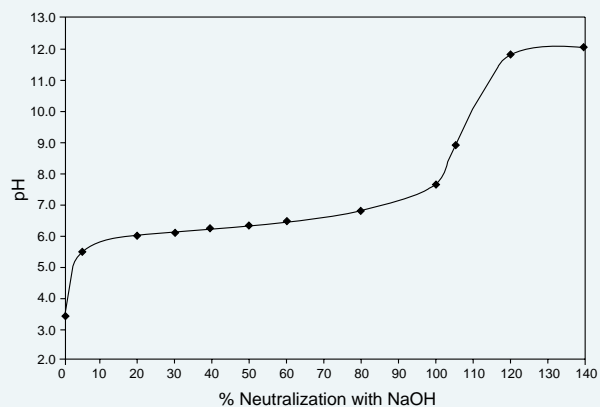


Figure 20—pH as a function of theoretical % neutralization for dispersions and solutions of 9823 HASE thickener.

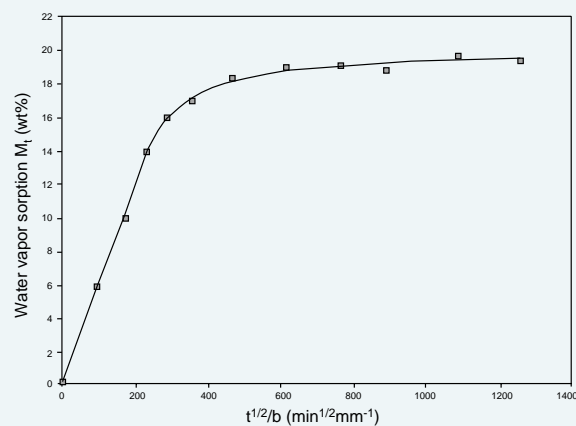


Figure 23—Moisture sorption curve at 23.0°C for unneutralized HASE thickener 9823 (dry film weight 0.50 g, film thickness b approximately 0.41 mm).

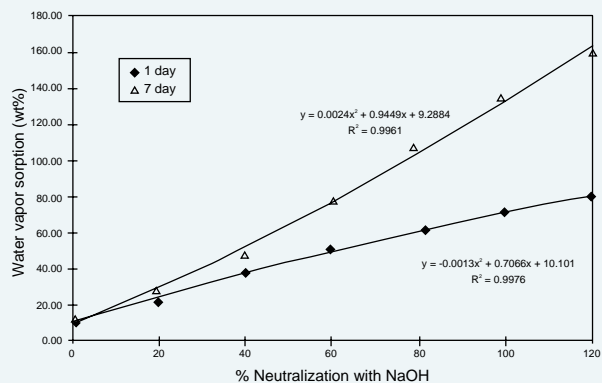


Figure 21—Effect of % neutralization of HASE thickener 9823 with NaOH on moisture sorption at 23.0°C—dry film weight 0.5 g dried 24 hr at 95°C.

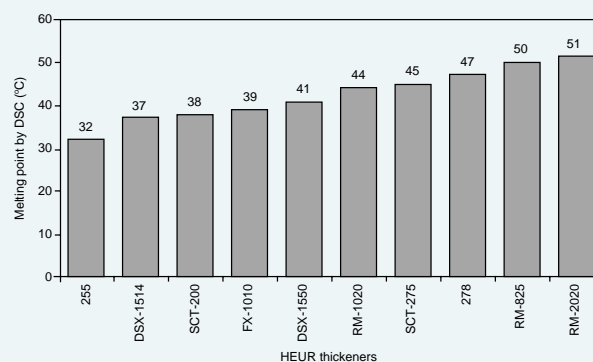


Figure 24—Thickener (HEUR) with melting points.

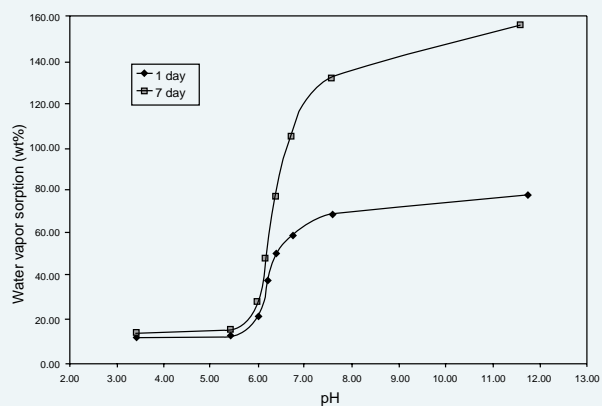


Figure 22—Effect of HASE thickener 9823 solution pH on moisture sorption at 23.0°C—dry film weight 0.5 g dried 24 hr at 95°C.

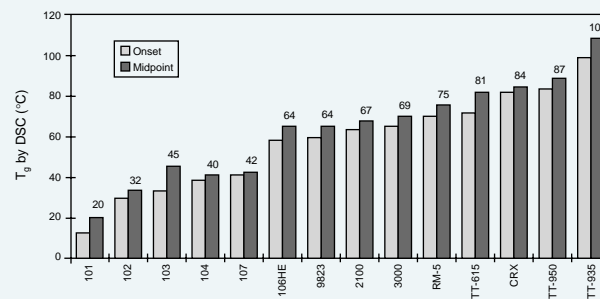


Figure 25—Thickener (HASE) with glass transition temperatures.



Figure 26—Moisture sorption cell using optional petri dish. Blisters in film are visible after one day at 23.0°C due to high WVS.

polymer ($D = 3.02 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1}$) where M_s was 19.05 g/g dry polymer, and the average film thickness b was 0.0158 cm. Using equation (4), the partition coefficient K was also obtained ($K = 0.187$) where densities for water and polymer were 1.00 g/cm³ and 1.21 g/cm³, respectively. In more practical terms, 18.7% of the sorbed polymer was water by volume at saturation.

Molecular Weight

For a given polymer type, WVS did not appear to be a function of molecular weight. This conclusion is drawn primarily from the cellulosic polymers tested (see Table 6). The two percent solution viscosities of the five sets of cellulosic thickeners compiled in this table reflect increasing molecular weight within each set. From the WVS compiled in Table 6, it is apparent that effect of MW is minimal. This result is what would be expected for polymers of relatively high molecular weight below the glass transition temperature (T_g) where chain and segment mobility is limited.

Other Film Properties

On visual inspection, the film forming properties of the thickeners tested for WVS varied considerably, but usually not to the degree where WVS would be affected due to edge effect from shrinkage, cracks, or holes. These latter problems were mostly avoided by careful drying of the samples at elevated temperatures below the boiling point of water and any other volatiles present. However, because some films were still imperfect, accuracy of the WVS determination was less certain in those cases. In general, film integrity was of the order ASE/HASE > HEUR/HENN (HNS) > cellulosics. At the extremes, some of the cellulosic thickeners were opaque and showed shrinkage with occasional cracks or defects, while most of the alkali-swellable thickeners formed clear continuous films. The nonionic synthetics thickeners (HNS) were somewhat intermediate forming continuous films which were usually opaque with a waxy or crystalline appearance. On drying and removal from an oven, the HNS polymers were often liquids, and on cooling, they solidified into waxy films.

DSC conducted on several of the alkali-swellable and HNS polymers showed that the ASE/HASE have T_g s, and the HNS, being of much lower molecular weight, have true melting points (see Figures 24 and 25).

Another noteworthy observation made was that some of the films having a combination of good film integrity and high moisture sorption actually formed blisters in the WVS cells, often in as little as one day. Figure 26 shows an example of this using the optional petri dish as the film substrate where blisters are readily visible. Occasionally, individual blisters were as large as half the dish surface area. On longer exposure times, the blisters would usually collapse presumably due to continued plasticization of the films with water. Besides the various film defects previously mentioned, the presence of blisters would be another source of error in WVS determinations. The degree of error is expected to be slight, but is presently unknown.

SUMMARY AND CONCLUSIONS

A relatively simple yet sensitive method was developed based on water vapor sorption (WVS) to individually examine the moisture affinity of film forming water-soluble and water-insoluble coatings additives. Except for the requirement of an oven and analytical balance, the technique used only readily obtainable, low-cost disposable components for moisture cell construction. In this study, a broad spectrum of thickeners was initially examined to determine the efficacy of the procedure and to quantify the relative moisture affinity of the polymers tested. The following are some of the more significant conclusions obtained:

- (1) The method was applicable to nearly all thickeners tested, and significant measurable response with good repeatability was obtained at ambient temperature in as little as 24 hr;
- (2) Control of film weight and to a lesser degree, temperature, were desirable for improved accuracy of test results;
- (3) A high degree of WVS differentiation was obtained between thickener samples (as much as 10X depending on the test time frame);
- (4) The acid form of the ASE and HASE thickeners showed much lower WVS than other thickener types. Being

Table 6—2% Solution Viscosities of Cellulosic Thickeners

Product Code	Product Type Supplier Code	Midrange Viscosity 2% Solution	WVS 2 Weeks
QP300	HEC - 11	275	121
ER4400	HEC - 11	5,000	121
ER52M	HEC - 11	50,000	126
QP100M	HEC - 11	110,000	118
250MBR	HEC - 2	5,500	103
250MBR	HEC - 2	28,000	101
E351	EHEC - 3	5,000	118
E481	EHEC - 3	80,000	116
7MT	CMC - 2	350	114
7M31T	CMC - 2	1,650	116
J5MS	HPMC - 5	5,000	96
J75	HPMC - 5	75,000	94

water-insoluble in this state, equilibrium saturation was obtained permitting estimation of diffusion coefficients. By definition, most of the other polymers were highly water-soluble tending toward infinite dilution rather than equilibrium saturation;

(5) The general order of moisture affinity obtained was alkali-swellable (acid form) << nonionic synthetics (HNS) < cellulosics \equiv alkali-swellable (salt form);

(6) The moisture affinity of alkali-swellable polymers increased linearly with increasing degrees of neutralization. Non-volatile bases (e.g., Na^+ and K^+ ions) at full neutralization gave high moisture affinity similar to the cellulosic thickeners regardless of dry time or drying temperature. Volatile bases gave variable response of lower degree depending on the amount of base remaining in film; and

(7) When a volatile base such as NH_3 or aminoalcohol was used to neutralize ASE and HASE thickeners and sufficiently dried to remove all of the base, very low WVS was obtained similar to that of the acid emulsion form of the same polymers.

Although no attempt has been made in this study to correlate WVS with actual coating performance, this is a natural extension and the ultimate objective of this work. However, a foundation has been provided for examining the moisture affinity of virtually all film forming components present in a coating including most thickeners, rheology modifiers, dispersants, and latex binders. The method may even lend itself to examination of formulated coatings. The results obtained suggest that with proper formulating technique, the alkali-swellable thickeners could ultimately provide the lowest degree of water sensitivity in coatings.

ACKNOWLEDGMENTS

The authors would like to express their appreciation to P. Bowden for FTIR examination and DSC analysis of the polymer tested, to Dr. M. Balik, North Carolina State University, for his consultation on moisture sorption theory, and to Dr. D.R. Bassett for his support of this project and paper.

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Appendix

List of thickener and rheology modifier suppliers for Tables 3a and b:

Reference No.	Supplier Company
1.	Allied Colloids, Coatings and Specialties Div.
2.	Aqualon Co.
3.	Berol Nobel, Nobel Industries
4.	Coatex, S.A.
5.	Dow Chemical U.S.A., Specialty Chemicals Dept.
6.	Henkel Corp., Coating Chemicals
7.	Kelco, Division of Merek & Co., Inc.
8.	National Starch and Chemical Co., Alco Chemical Div.
9.	RHEOX, Inc.
10.	Rohm and Haas Co.
11.	Union Carbide Corp.