Quantitative Method for Determination of Thickener Equilibration in Coatings

Greg D. Shay, Keith R. Olesen, and David L. Hardman—Union Carbide Corp.*

A quantitative method for the determination of thickener incorporation rates and thickener equilibration times (TET) in coatings has been developed using a digital Krebs viscometer. Upon adding thickener to a coating sample, the viscometer simultaneously provides viscosity readout and continuous mixing at constant speed with degree of agitation simulating the relatively poor mixing conditions observed in some paint production equipment near the end of the process cycle. By plotting viscosity as a function of mixing time on the instrument, rates of incorporation and equilibration were obtained. The method proved to be reliable and generally reproducible in limited testing with apparent applicability to a variety of thickener types in both aqueous solution and in actual latex coating formulations. Meaningful comparisons of incorporation are now possible to facilitate appropriate thickener selection and to provide insight regarding optimal modes of incorporation or orders of addition for process cycle time reduction.

INTRODUCTION

Viscosity is a quality control or sales specification for many waterborne formulations including paints, paper coatings, adhesives, caulks, drilling fluids, shampoos, inks and the like. Common to these formulations is the presence of thickeners, which are incorporated to provide the viscosity for which a specification range is assigned. In coatings formulations, viscosity specifications may be established at more than one shear rate to define rheology requirements (e.g., at low-shear for leveling or sag resistance mid-shear for mixing and pumping, or at high-shear for brush drag and film build).[1-3] If only one viscosity specification is assigned, it is usually in the mid-shear rate range of 10-1000 sec^{-1} as determined on a Brookfield (Brookfield Eng. Lab., Stoughton, MA), Rotothinner (Research Equipment Ltd., Hampton Hill, England), or, more frequently, a Stormer (BYK-Gardner USA, Silver Spring, MD) type rotational viscometer. The coating viscosity measured on these instruments is often referred to as the paint's "consistency,"[4,5] and the test procedure for this determination using a Stormer viscometer is defined in ASTM standard D 562-81.[6]

During the course of coating development, several questions may arise: (1) When has full viscosity been developed in the formulation?; (2) Does order of addition or mode of thickener incorporation make a difference?; and (3) Are there ways to incorporate thickener to reduce processing time? In recent years, there has been an increased emphasis on reducing the development time for new product introductions, and consequently, these questions may go unanswered due to uninformed choices or lack of time for thorough investigation. However, there has also been recent emphasis on process cycle time reduction. It is not enough that a given formulation just meet performance requirements, it should also be optimal with regard to scaling, reproducibility, and efficient processing in production. Thickener incorporation can have a significant impact on all of these parameters.

One obstacle that has made meaningful and timely comparisons of thickener incorporation difficult is the lack of a simple laboratory method for characterization. Thus, an objective of the work presented in this paper is to provide formulators with a convenient method for observing rates of thickener incorporation and for quantifying equilibration times under conditions simulating the relatively poor mixing that may be encountered in some production equipment near the end of a process cycle. Using the new test procedure and data generated, informed options and guidelines for thickener selection and best mode of incorporation hopefully will be revealed. For purposes of determining the efficacy of the technique, emphasis was placed on aqueous solutions and pigmented architectural coatings.

---

*UCAR Emulsion Systems, 410 Gregson Dr., Cary, NC 27511.

Table 1—Thickener Types Commonly Used in Waterborne Coatings

Inorganic Thickeners
- Attapulgite and bentonite clays
- Fumed silicas

Cellulosic Thickeners
- Hydroxyethyl cellulose (HEC)
- Ethylhydroxyethyl cellulose (EHEC)
- Hydrophobe modified HEC (HMHEC)

Nonionic Synthetic Thickeners
- Hydrophobe modified ethoxylate urethanes (HEUR)
- Hydrophobe modified EO or EO/PO ureas, urethane/ureas, and ethers

Alkali-Responsive Thickeners
- Alkali-swellable/soluble emulsions (ASE)
- Hydrophobe modified ASEs (HASE)

Thickener Types and Incorporation Options

Several types of thickeners are used in waterborne coatings,[7-9] and different methods or orders of addition for incorporation are often used for each depending on their physical form or the chemical nature of the product (*Table* 1). Hydroxyethyl cellulose (HEC) and its associative derivatives are among the most popular thickeners used in coatings. These and other polysaccharide thickeners are normally supplied as powders, and when employed, they are often placed in the pigment grind for ease of incorporation. As post-adds, these and powdered inorganic thickeners can be more problematic than those supplied as liquids. To improve upon this, slurries or low solids aqueous stock solutions of these thickeners can be prepared in advance if sufficient water is available from the coating formula. Fluidized versions of some associative and non-associative cellulosic thickeners are also available commercially and may be advantageous.

Another type of thickener often employed in aqueous coatings is non-ionic associative synthetic polymers. The most common of these are the hydrophobe modified ethoxylate urethane (HEUR) thickeners and similar ethylene oxide and ethylene oxide/propylene oxide products containing urea, urethane-urea, or ether linkages. The nonionic associative polymers are mostly supplied in water or more often in water/cosolvent blends. Because they are supplied in solution form, most are viscous and can take a relatively long time for complete dispersion in a coating and for full viscosity development.

The third primary class of thickeners used in aqueous coatings are the alkali-swellable/soluble emulsions.[10] These products are sometimes referred to as alkali-responsive thickeners and consist of two basic types: the conventional variety (ASE), and the associative variety, which are hydrophobe modified (HASE). Subclasses of HASE are defined based on the coupling functionality of the associative unit to the main chain, which is usually urethane or ester linkages. All alkali-responsive polymers require neutralization with a suitable base for conversion of the low viscosity latex emulsion into a water soluble thickener. The neutralization is normally done after adding the thickener emulsion to the coating, and thickening occurs upon dissolution if the polymer is truly soluble, or on swelling if it is lightly crosslinked. With the requisite amount of base, the inversion process is very rapid, and the “equilibration time” for full viscosity development can be quite short relative to other thickener types. This feature of alkali-responsive thickeners is highly desirable for process cycle time reduction, but to obtain full advantage, the more numerous incorporation options for these thickeners must be carefully considered. A method to quantify incorporation would help facilitate making the appropriate choices for process optimization.

Thickener Equilibration

Thickener equilibration time (TET), as defined here, is the time required for full viscosity development after thickener incorporation (i.e., the time it takes for no further change in viscosity on continued mixing). For comparative purposes, this determination ideally should be made under controlled conditions of mixing speed, temperature, container size, fluid volume, and similar pH. Since thickeners vary widely in their thickening efficiencies, the amount of each thickener incorporated should also be adjusted to maintain the same equilibrated viscosity (consistency) for meaningful comparison as determined on a mid-shear rate viscometer. The amount of thickener required for the target viscosity can be determined using multiple trials. However, two trials are often sufficient with one higher and one lower than the target value with the required thickener level determined by interpolation.

Most paint laboratory bench mixers have blade configurations and speed capability which provide very efficient mixing and a good vortex during thickener equilibration. With variable speed control, the formulator’s temptation is to operate at optimum mixing conditions (i.e., adjust speed during processing to maintain a good vortex without air entrainment). Consequently, lab mixers operated in this fashion may not simulate actual production. This is particularly true near the end of the paint processing cycle when the let-down tank is full, and there is little or no vortex present in some production equipment. Although the agitation could be moderated to reduce the vortex, a significant limitation of the common lab stirrer is its inability to measure viscosity while mix-

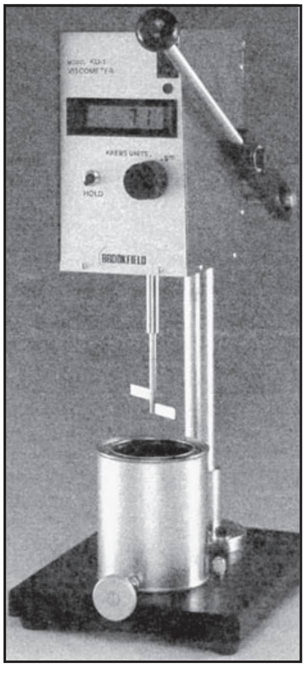

Figure 1—Brookfield KU-1 viscometer with standard Stormer type spindle for continuous mixing and simultaneous Kreb’s viscosity determination.

ing. To determine thickener equilibration, several trips to a Stormer or other mid-shear rate viscometer would be required to ensure that there was no further change in viscosity. This procedure would be rather tedious. Therefore, many formulators prefer to mix the final paint for a few minutes and let the sample set overnight on the assumption that it will be fully equilibrated on the following day. A Stormer viscosity is then obtained to determine consistency, and samples may then be retained for determination of room temperature stability, roller stability, and oven heat age stability. If there is an increase in the Stormer viscosity in these aging tests, this is normally attributed to some type of coating instability. But there is always a lingering question: was the thickener fully equilibrated before the aging tests were started? If the thickener was not fully dissolved or swollen, or if thickener gel particles were still present, the initial viscosity obtained would have been lower than that for full equilibration resulting in a misleading conclusion on coating stability.

EXPERIMENTAL

One of the primary objectives in this project was to develop an equilibration test method which: (1) employs a viscometer commonly used in coatings laboratories for measuring paint consistency; (2) would permit continuous mixing and viscosity measurement simultaneously; (3) would simulate the poorer mixing conditions of some production equipment; (4) would provide data on the rate of thickener incorporation; (5) would leave no uncertainty about when the coating viscosity is equilibrated; and (6) could be completed in a reasonable period of time. With this method, the effects of incorporation mode, order of addition, thickener types, binder interactions, and other coatings variables could then be examined quantitatively.

A convenient instrument chosen which meets these criteria and one that is often used for a quality control and formulation development is the Brookfield KU-1 digital viscometer (*Figure* 1). Using a small paddle identical to that on a Stormer viscometer for Krebs viscosity determination, this instrument mixes the sample at a constant speed of 200 rpm while torque and viscosity are measured.[11] The viscosity range capability of the instrument is 53 to 140 Krebs Units (KU) in 1 KU increments with interpolation to 0.5 KU possible.

A 250 ml beaker or a one-half-pint-lined paint can containing about 150 ml of liquid was used for aqueous solution and paint test samples respectively. These containers are approximately the same diameter, and with two standard support pods or an adjustable lab jack under the container, the spindle mark is positioned at the liquid surface for accurate viscosity readings while mixing. Prior to adding thickener, mixing with the KU-1 viscometer is generally very good, and a moderate vortex observed. As viscosity develops during and after the addition of thickener, the vortex usually disappears, but sufficient movement exists at the surface and particularly within the fluid for adequate turnover. We believe this later stage of mixing simulates the relatively poor mixing conditions found in some production equipment.

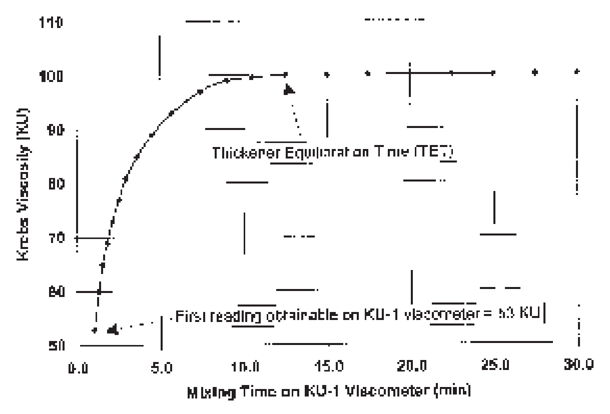

Figure 2—Sample thickener incorporation profile for determination of TET on the Brookfield KU-1 viscometer–thickener amounts added to give 100 KU at TET.

Trial runs for each different thickener or mode of incorporation were initially conducted to determine the amount of thickener required for the same equilibrated Krebs viscosity, which was arbitrarily chosen to be 100 KU for most experiments. To ensure full neutralization of ASE and HASE type thickeners, base amounts were calculated or experimentally predetermined to give pH values between 8.5-9.5, which is in the middle of the rather broad range where viscosity is independent of pH for most alkali-responsive thickeners. The pH was measured following the equilibration test to confirm that it was in the specified range.

Test runs were conducted at room temperature typically at 20 or 23°C. In some phases of the investigation, a jacketed beaker connected to a temperature controlled circulator was used for more precise determinations. During run times in excess of an hour, aluminum foil was placed over the containers with a small hole in the center to accommodate the viscometer spindle. This minimized evaporation of volatile components (mostly water), which would have resulted in a gradual increase in viscosity during long runs.

The small amount of heat produced due to mixing at the relatively low rpm of the instrument was apparently dissipated throughout the runs. This conclusion is based on the temperature difference recorded (typically <0.2°C) between sample and surrounding air over a three hour period for several equilibrated samples at 100 KU viscosity. A slight temperature rise due to heat of neutralization was noted at the start of some ASE or HASE thickener runs. The degree of rise was a function of the amount of thickener required for the target KU viscosity and the thickener's acid content. The maximum temperature rise observed in aqueous solution was 1.9°C for a relatively inefficient HASE thickener, which required more base for neutralization; however, typical temperature excursions for most alkali-responsive thickeners were on the order of 0.3°C. No attempt was made to adjust this temperature, as this approximates what would have occurred in actual production. Sample temperature was normally back to ambient within about 30 min due to gradual heat loss to the environment.

Table 2—Interior Semi-Gloss Test Paint Formulation Used for Determination of Thickener Incorporation and Equilibration (20 PVC/30 NVV).

			100 gal Formula		1/2 Pt Test
Component	Function	Supplier	Mass (lbs)	Volume (gal)	Formula (g)
Grind					
Water			105.99	12.71	26.22
Polywet ND-35	Dispersant	Uniroyal	4.04	0.39	1.00
Ti-Pure R-902	Titanium dioxide	DuPont	207.20	6.30	51.25
Drew L-475	Defoamer	Drew	2.02	0.26	0.50
Letdown					
Water			33.68	4.04	8.33
UCAR 367	V/A latex	Union Carbide	427.53	47.50	105.76
UCAR Filmer IBT	Coalescent	Union Carbide	24.01	3.03	5.94
Nuosept 95	Preservative	Hüls	2.02	0.21	0.50
Triton GR-5M	Surfactant	Union Carbide	1.01	0.12	0.25
AMP-95	Buffer	ANGUS	5.05	0.65	1.25
Drew L-475	Defoamer	Drew	4.04	0.54	1.00
Grind + Letdown			816.61	75.76	202.00
Post Adds					
Thickener	*thickener amount for 100 KU		A	A	*A
Ammonia (28%)	*base adjustment for pH 9		B	B	*B
Water	*water adjustment for 50 g total		C	C	*C
A+B+C			202.14	24.23	60.00
Total			**1010.27**	**100.00**	**262.00**

Detailed Procedure for Aqueous Solutions

For determination of TET in aqueous solution in the absence of other coating components, 250 ml beakers normally containing 150.0 g total charge of deionized water, thickener, and neutralizing base were used to allow unobstructed observation of the samples during the test runs. Charges of 200 g were used in some of the earlier experiments. One of the important parameters studied for alkali-responsive thickeners was order of addition for base and thickener. In the "base in first" scenario, the water and neutralizing base were charged to the beaker and placed on the viscometer. After stirring was started, the thickener was added by syringe between the spindle and beaker wall over 15 sec. The end of the 15 sec interval was taken as "time 0" for determination of TET, and viscosity readings were then recorded periodically until equilibration. In the "base in last" method, water and thickener were charged to the beaker followed by base addition by syringe over 15 sec. As with the previous order of addition, viscosity readings were taken periodically until no change was observed. On plotting the viscosity versus time, rate profiles were obtained, and the first occurrence of a constant reading was recorded as the TET (*Figure* 2).

Table 3—Code Key for Commercial Thickeners Appearing in Text, Tables, and Figures

Thickener	Code
UCAR® Polyphobe® 102	HASE A
UCAR® Polyphobe® 104	HASE B
UCAR® Polyphobe® 107	HASE C
UCAR® Polyphobe® TR-116	HASE D
UCAR® Polyphobe® 9829	HASE E
Acrysol® TT-615	HASE F
Acrysol® TT-935	HASE G
Acrysol® RM-825	HEUR A
Acrysol® SCT-275	HEUR B
Natrosol® Plus® 330	HMHEC A
Natrosol® FPS Plus® 330	HMHEC B

UCAR® Polyphobe® is a trademark of the Union Carbide Corp.
Acrysol® is a trademark of The Rohm and Haas Co.
Natrosol® Plus® and FPS Plus® are trademarks of Aqualon Corp.

Detailed Procedure for Pigmented Coatings

The pigmented coating used in this work was a 20% pigment volume concentration (PVC), 30% nonvolatile by volume (NVV) interior semi-gloss vinyl-acrylic latex formulation as shown in *Table* 2. For the determination of TET in this test formulation, one-half-pint-lined paint cans were used containing 202.0 g of unthickened paint consisting of the pre-dispersed pigment grind plus latex letdown. Held out of each can for thickener incorporation was a combined total of 60.0 g water, thickener, and ammonia for neutralization and pH adjustment if required. Some AMP (amino methyl propanol) was initially present in the original unthickened paint for stability; however, the amount of this alkaline base ordinarily was not sufficient for full neutralization (pH 8.5-9.5) of the ASE and HASE thickeners tested. The order of addition scenarios and procedures described for aqueous solutions were also employed in evaluation of the pigmented coatings. The commercial thickeners examined in the test formulation for method development are shown in (*Table* 3), where they are coded for reference in the text, tables, and figures that follow.

RESULTS AND DISCUSSION

Initial thickener equilibration test data was obtained using simple aqueous solutions consisting of deionized water, thickener, and neutralizing base when required. Some of the parameters examined in aqueous solution were the constancy of KU value on equilibration, test repeatability, effect of temperature, effect of thickener efficiency, and effect of thickener type. The previously described commercial paint formulation was used in subsequent testing to evaluate the efficacy of the thickener equilibration procedure under more realistic conditions. Using the vinyl acrylic test paint formulation and the procedure for pigmented coatings detailed, the effects of neutralizing base order, thickener type, thickener pre-dilution, and thickener concentration, were examined.

In general, the results obtained for rates of incorporation and equilibration in the test paints were similar to those obtained in aqueous solution. However, when thickener gel particles occasionally occurred, they were less visible in paints but could be seen in the slow moving liquid surface. In aqueous solution, the beakers provided high visibility due to the initial opacity of the seeds. As the gel particles became more swollen prior to complete dissolution, they became transparent and more difficult to see. An example of gel seeding on initial incorporation of thickener is shown in *Figure* 3.

Though rare, a more severe response on addition of thickener to the test paint was the formation of lumps which in extreme cases had the appearance of cottage cheese. On mixing, the lumps were eventually reduced to seeds and with further mixing disappeared completely. This was evidence that the seeding phenomenon was due to thickener gel particles rather than due to agglomerated pigment or latex. The latter conditions are not easily reversible particularly under the relatively poor mixing conditions which existed on the viscometer.

Another advantage of conducting equilibration tests in aqueous solution was the observance of "rod climbing" when it occurred. This rheological phenomenon is the well known Weissenberg Effect[12,13] and is due to normal forces acting on the fluid due to the polymer's elastic component of viscoelasticity. An example of this occurrence with a HEUR thickener prior to equilibration is shown in *Figure* 4.

Effect of Thickener Concentration in Paint: The importance of conducting thickener comparisons at the same Krebs viscosity was demonstrated by incorporating different amounts of the same thickener (HASE D) in the test paint samples with the neutralizing base in prior to thickener addition. An example of the effect on final viscosity and TET is shown in *Figure* 5. Equilibrated viscosity was directly related to the amount of thickener present as expected; however, the TET was inversely proportional to thickener concentration for the majority of thickener types tested. Thickener concentration data obtained for several different products are compiled in *Table* 4.

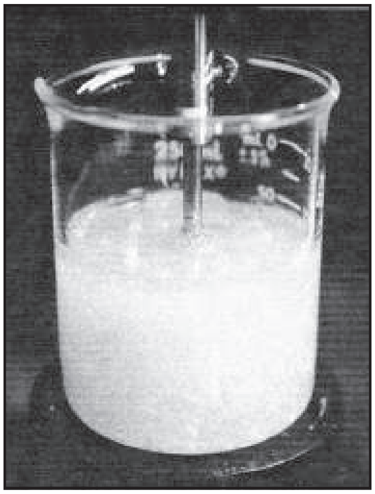

Figure 3—Gel particle formation on rapid neutralization of a high molecular weight ASE thickener in aqueous solution.

Effect of Temperature: The effect of temperature on TET was evaluated using HASE D without thickener dilution and the "base in first" order of addition. Although the equilibrated viscosity was inversely proportional to temperature as would be expected, temperature had almost no effect on TET (approximately eight minutes) in this example over the modest temperature range studied (*Figure* 6). Based on these results, determination of TET at room temperature would be at least semi-quantitative and acceptable for most determinations. Temperature control with a jacketed beaker is recommended for more precise results particularly when comparing the magnitude of the viscosity developed.

Procedure Repeatability in Aqueous Solution: Repeatability of the test procedure was conducted on a limited basis with one thickener sample (HASE D) in aqueous solution as shown in *Figure* 7. The duplication of incorporation profiles was excellent for the first two runs (Run #1 and #2), which were conducted on the same day where the equilibration times and equilibrated viscosities obtained were essentially identical. The single run on the second day was only 1 KU unit higher (within measuring repeatability of the instrument) with a somewhat longer equilibration time possibly due to a difference in room temperature. Although other data not shown here gave confidence in the relative repeatability of the test method, further studies are recommended in both aqueous solution and in paint samples to establish reproducibility with a variety of thickeners covering a broad range of equilibration times.

Effect of Thickener Addition Rate: The effect of thickener addition rate on incorporation and TET was examined in aqueous solution using thickener HASE B with "base in first." As this was one of the earlier experiments, a higher amount (208 g) of total solution was used rather than the later stan-

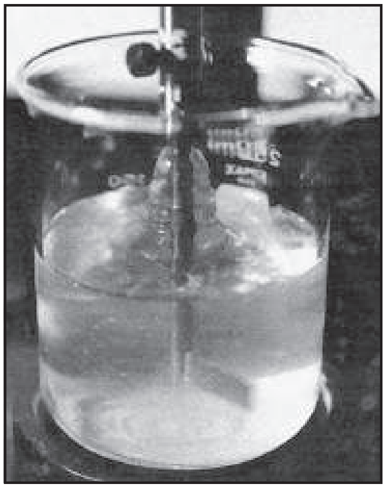

Figure 4—Observation of "rod climbing" during equilibration of a HEUR thickener sample in aqueous solution.

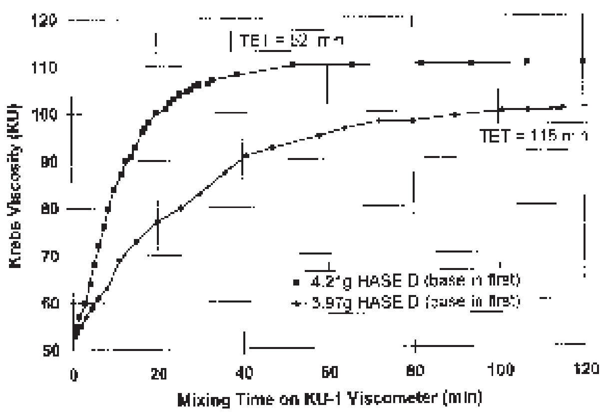

Figure 5—Effect of thickener concentration on viscosity and TET for HASE D in test paint formulation.

Table 4—Effect of Thickener Concentration on TET in Test Paint Formulation

HASE Thickener	Amount (g wet)	Equilibrated Viscosity (KU)	TET (min)
HASE C	5.49	90	210
	6.02	99	92
HASE D	3.97	101	115
	4.21	110	52
HASE F	3.53	92	620
	3.79	102	355
HASE G	4.72	98	100
	5.22	117	90
HASE E	5.13	104	112
	5.97	124	100

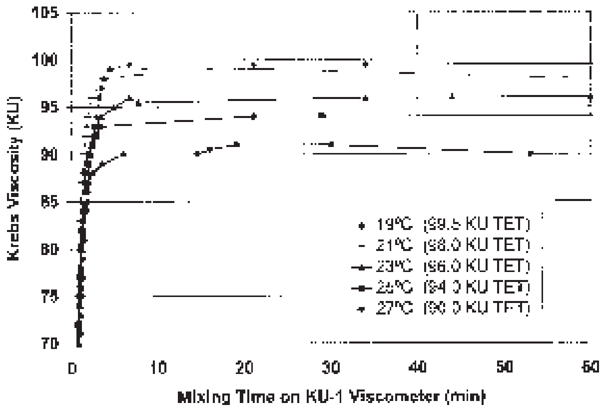

Figure 6—Effect of temperature using temperature control with a jacketed beaker (equilibration KU in legend are at 60 min mixing time).

dard which was set at 150 g. Compared was the rapid injection of 7 ml of 25% thickener emulsion versus adding the same amount dropwise over 30 sec. Clearly, a longer addition time provided improved incorporation resulting in faster equilibration. TET for the dropwise addition was 190 min versus about 400 min for the rapidly injected fluid (*Figure* 8). The "spike" in viscosity observed within the first 10 min of the runs in *Figure* 8 is believed to be due to a momentary concentration of thickener around the agitator blade on initially being pulled into the paint from the surface. The thickener then disperses with a resultant viscosity drop and then gradually increases during the equilibration process.

EFFECT OF THICKENER TYPE IN AQUEOUS SOLUTION: Three associative thickeners of distinctly different chemical composition (HASE D, HEUR B and HMHEC A) were successfully tested in aqueous solution on the KU-1 viscometer demonstrating that the procedure is applicable to a variety of thickener types (*Figures* 9 -10). The "base in last" method was used for the HASE thickener, and two drops of ammonia were added to the water for efficient incorporation of the HMHEC. More importantly, these runs showed that the method can be used as a means of thickener comparison for rate of incorporation and TET. The data generated also suggest that TET may not be the only criteria which should be considered for thickener selection. In some instances, the "rate of initial incorporation" may be considered more important than the final equilibration time. As a case in point, the HASE thickener actually produced semi-equilibrated KU about 10 times faster than the HMHEC, even though the HASE TET was approximately three times longer (60 min vs 20 min).

The HEUR product tested produced a very unusual profile with an initial peak at 107 KU followed by continued reduction in viscosity over about nine hours with a final equilibration value at 86 KU (*Figure* 10). Like many HEUR products, this thickener is supplied as a viscous solution in water/Butyl Carbitol cosolvent. The cosolvent is present to increase solubility of the polymer and to disrupt association thereby minimizing viscosity. Because this polymer has a low molecular weight with little contribution to hydrodynamic thickening, we believe the initial rise in KU was due to increased intermolecular association, which occurred on significant reduction of the cosolvent/water ratio, when the thickener was added to the water. The subsequent drop in viscosity may have been due to gradual repartitioning of water, cosolvent, and polymer. When a different HEUR thickener was tested, which was supplied in water only, the incorporation profile obtained was similar to that of the HMHEC thickener.

INSTRUMENT AND VISCOSITY STABILITY IN AQUEOUS SOLUTION: The instrument reliability and viscosity stability on mixing times are evident in *Figure* 10 for the HASE D and HMHEC A thickener samples tested. The equilibrated viscosities remained constant at 100 KU and 102 KU, respectively, for over 12 hr demonstrating the instrument is capable of sustained operation. These results also show that once the samples are equilibrated, the viscosity does not change if the coating has inherent stability.

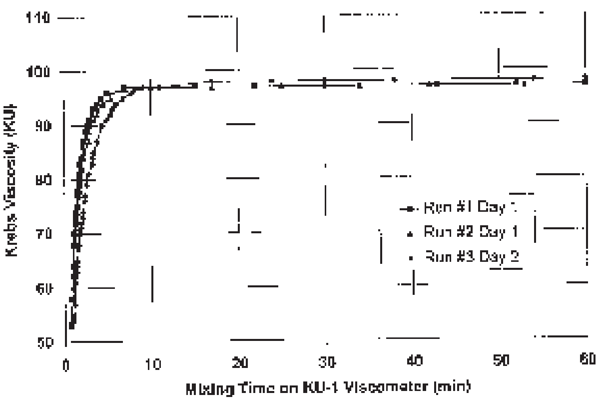

Figure 7—Incorporation profiles for repeatability determined on HASE D without temperature control in aqueous solution using "base in first" method.

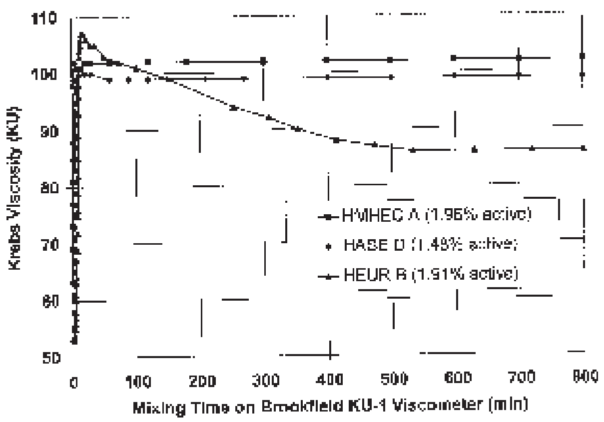

Figure 10—Twelve hour profiles for incorporation tests shown in Figure 9.

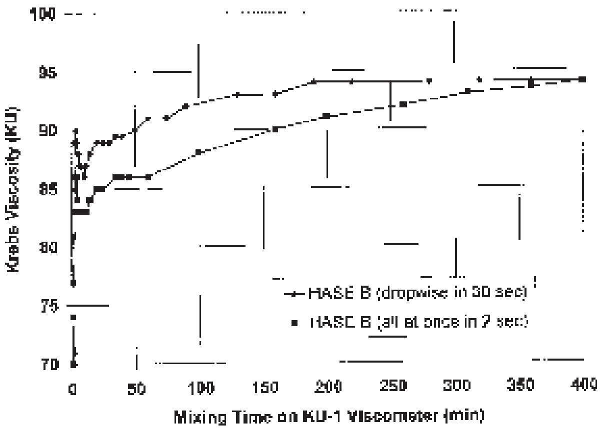

Figure 8—Effect of thickener addition rate for HASE B using "base in first" order of addition (200.0 g water, 1 ml ammonia, 7 ml HASE at 25% solids).

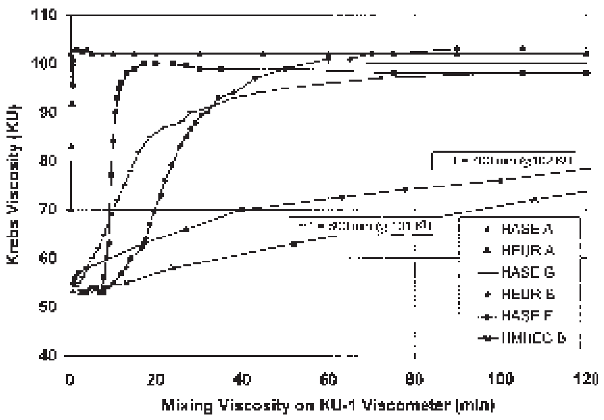

Figure 11—Incorporation profiles for several thickener types in test paint formulation–"base in first" order of addition for the three HASE thickeners examined.

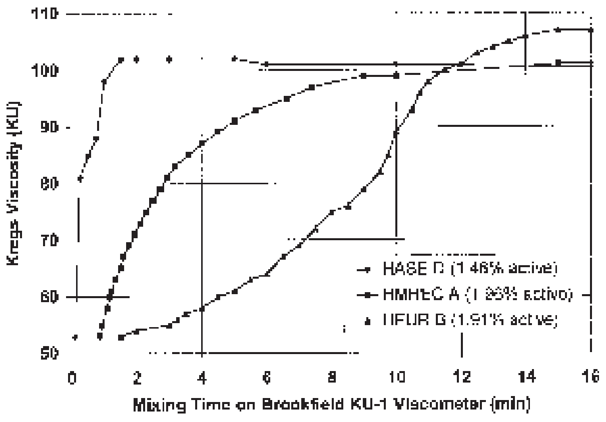

Figure 9—Thickener incorporation profiles for HASE D in aqueous solution with ammonia neutralization to pH 9 (first 16 min of a 12 hr run).

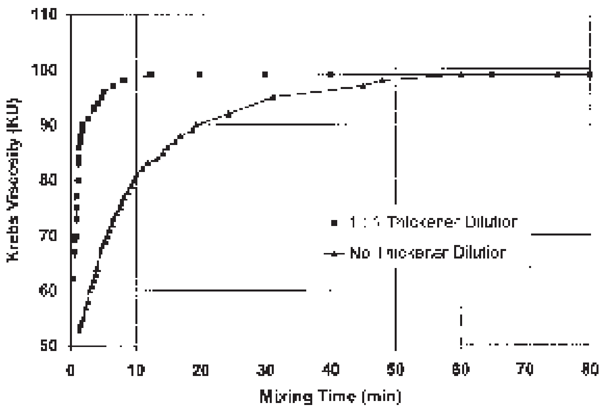

Figure 12—Effect of water dilution on rate for HASE D thickener in the test paint formulation using "base in first" order of addition (0.62% active thickener in coating).

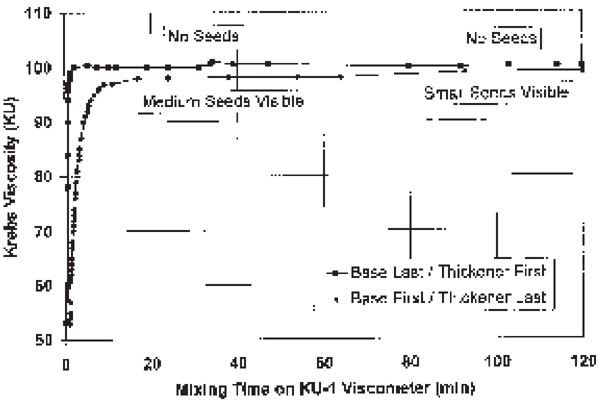

Figure 13—Effect of base/thickener post-addition order on equilibration of HASE D in aqueous solution (143.8 g deionized water, 1.01 g 28% ammonia for pH 9.7, 5.25 g 40% HASE D for 1.38% active in final solution).

Effect of Thickener Type in Pigmented Coatings: A representative sample of thickener types was examined in paint. Included were several HASEs, HEURs, and HMHEC. The wide variations in incorporation profiles and TETs are shown in *Figure* 11 and *Table* 5 respectively.

Although the magnitude of difference in incorporation rates and equilibration times observed in *Figure* 11 was surprising, the relative order for the different thickeners was generally what might be intuitively expected based on what is known about their physical and chemical natures.

It is known that products of a given class with higher thickening efficiencies tend to be of higher molecular weight or with more swellable character. Consequently, these products might be expected to be more difficult to incorporate and thus, have longer equilibration times. This was basically what was observed as shown in *Table* 5, e.g., the TET for HASE A (4.48 g active) was less than HASE G (1.42 g active) was less than HASE F (1.14 g active). Similarly, TET for HEUR A (2.01 g active) was less than HEUR B (1.75 g active). Products supplied as solutions or dispersions with higher viscosities also might be expected to have longer equilibration times since these products would be expected to disperse more slowly. Comparative examples of this phenomenon here were: TET for HEUR A (2000 cps) was less than HEUR B (3000 cps) was less than fluidized HMHEC B (7000 cps). The cellulosic product may have had additional contribution to long equilibration time due to its high molecular weight relative to the HEURs, or due to its higher density which is a result of salts present in the product to suppress hydration. Being more dense, this thickener tended to sink quickly to the bottom of the test container, which may have made it more difficult to disperse.

Table 5—Effect of Thickener Type, Thickener Efficiency (Active Concentration), and Supplied Viscosity on TET in Paint Test Formulation

Thickener	Supplied Viscosity (cps)	Amount wet (g)	Thickener Solids (%)	Amount Active (g)	TET (min)
HASE A	30	17.92	25.0	4.48	5
HEUR A	2000	8.04	25.0	2.01	80
HEUR B	3000	10.00	17.5	1.75	90
HASE G	30	4.72	30.0	1.42	100
HASE F	30	3.79	30.0	1.14	400
HMHEC B ...	7000	7.13	25.0	1.78	800

Mean and standard deviation data for 30 different equilibrated thickener samples of various thickener types at standard test conditions in paint were as follows: equilibration viscosity (101.4 ± 2.2 KU), TET (118 ± 169 min), active thickener concentration (0.80 ± 0.67% or 9.82 ± 8.26 g/L), change in KU after six months at room temperature (–0.22 ± 3.3 KU at pH of 9.34 ± 0.42).

Effect of Thickener Dilution in Paint: Production experience has shown that pre-dilution of alkali-responsive latex emulsions with water often helps speed thickener incorporation. We believe this is due to the size reduction or total elimination of thickener gel particles, which sometimes form when the thickener is added concentrated (typically 25-40% active). Using HASE D as a test model, a study was conducted to examine quantitatively the effects of latex thickener dilution at constant active thickener level. A comparison was made using the "base in first" order of addition with the standard total amount of water, neutralizing base, and thickener held out of the test paint (*Figure* 12). As noted there, the effect of thickener dilution was rather dramatic. A 1:1 dilution of the thickener with water reduced equilibration time from 60 min to about 15 min in this example.

Effect of Base Addition Order in a HASE Thickener: The order of addition for post-addition of neutralizing base and thickener was examined for HASE D thickener in aqueous solution using the procedure described previously. In this study the "base in last" method provided a much shorter TET with no visible seeding throughout

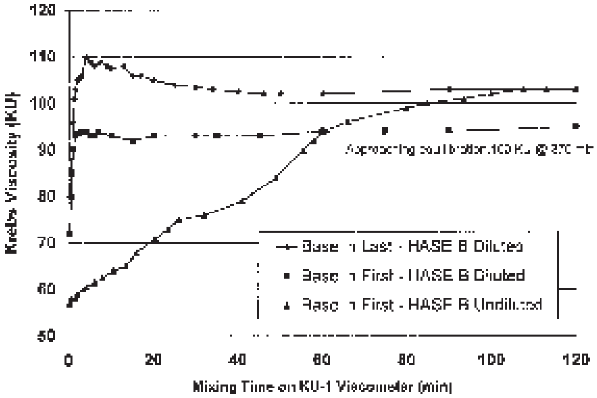

Figure 14—Effect of base/thickener addition for HASE B in test paint formulation (53.54 g deionized water, 5.44 g HASE B, 1.0 g ammonia).

the run (*Figure* 13). Although not shown, two other HASE thickeners were tested in aqueous solution with similar results.

On examination of base/thickener addition order in pigmented coatings, the results for incorporation of diluted HASE B in *Figure* 14 were similar to those obtained for addition of HASE D in aqueous solution (i.e., more complete incorporation was obtained with the "base in last" order of addition as indicated by a higher initial KU viscosity and a shorter TET). In both types of media, the thickener gel particles, which formed in the "base in first" order of addition, did so as soon as the thickener was added. With this order of addition, the initial KU value for the paint sample tested was about 10 units lower than for "base in last" method, and the gel particles which were present took over six hours for complete disintegration and equilibration. This example demonstrates that even a diluted thickener sample can be problematic with the "base in first" method if it thickens so quickly that gel particles form. This condition is of course aggravated with poor mixing conditions. Curiously, the undiluted sample with "base in first" actually produced a shorter equilibration time even though it had the expected slower initial rate of incorporation. Any thickener gel particles which may have formed there were apparently fewer, smaller or more easily dissolved. Order of base/thickener addition in HASE thickeners will be examined in much greater detail in a future publication. Although it appears that "base in last" is normally the preferred order of addition for alkali-responsive thickeners, the evidence obtained to data is insufficient for clear guidelines. The best mode of addition may be system dependent and warrants further study.

CONCLUSIONS

A simple quantitative method for the determination of thickener incorporation and equilibration in coatings has been developed, and its efficacy demonstrated. The studies conducted and summarized in this paper were not meant to be exhaustive, but they were useful for providing preliminary data and initial conclusions on the test method and on some of the many variables that can be examined using this technique. Among the conclusions and findings are the following:

(1) The test method uses instrumentation and measurement that are common standards for quality control of mid-shear rate viscosity in architectural coatings;

(2) The test method is simple, reliable, reproducible, and quantitative;

(3) The method generally simulates the relatively poor mixing conditions that have been observed in the final processing stages of some production equipment;

(4) Ambient temperature is sufficient for TET determination, but reproducibility of equilibrated viscosity values can be improved with temperature control;

(5) Most TETs can be obtained within two hours;

(6) Method is applicable to different types of thickeners and different modes of incorporation with variation in TET as much as 100X observed;

(7) HASE thickeners appear to provide some of the fastest TETs and incorporation rates;

(8) Slower addition of thickener reduces TET;

(9) Thickener dilution prior to incorporation can also significantly reduce TET;

(10) Best order of addition may be system dependent, but present evidence suggests that adding the neutralizing base last is more efficient for HASE thickeners; and

(11) As a general rule, higher efficiency thickeners and more viscous thickeners as supplied produced longer TETs for the same types of thickener.

References

(1) Sarkar, N. and Lalk, R.H., "Rheological Correlation with the Application Properties of Latex Paints," JOURNAL OF PAINT TECHNOLOGY, *46*, No. 590, 29 (1974).

(2) Dutt, N.V.K. and Prasad, D.H.L., "Relationship Between Rheological Properties and Paint Performance," *Pigment and Resin Technology*, pp. 10-18, January 1985.

(3) Fearnley-Whittingstall, P., "Paint Rheology," *J. Oil & Colour Chemists' Assoc.*, Vol. 10, pp. 360-368 (1991).

(4) Payne, H.F., *Organic Coating Technology*, Vol. II, "Pigments and Pigmented Coatings," John Wiley & Sons, Inc., New York, pp. 743-744, 1961.

(5) Eley, R.R., "Rheology and Viscometry," Chapter 33 in *ASTM Paint and Coatings Testing Manual: 14th Edition of the Gardner Sward Handbook*, Koleske, J.V. (Ed.), ASTM Manual Series MNL 17, pp. 359-360, 1995.

(6) *Annual Book of ASTM Standards*, Volume 06.01, "Paints, Related Coatings, and Aromatics," ASTM Designation D 562-81, pp. 95-97, 1993.

(7) Shay, G.D., "Thickeners and Rheology Modifiers," Chapter 30 in *ASTM Paint and Coatings Testing Manual: 14th Edition of the Gardner Sward Handbook*, Koleske, J.V. (Ed.), ASTM Manual Series MNL 17, pp. 269-270, 1995.

(8) Blake, D.M., "Thickeners for Waterborne Coatings," Chapter 4 in *Handbook of Coatings Additives*, Vol. 2, Calbo, L.J. (Ed.), Marcel Decker, pp. 43-117, 1993.

(9) Schaller, E.J. and Sperry, P.R., "Associative Thickeners," Chapter 4 in *Handbook of Coatings Additives*, Vol. 1, Calbo, L.J. (Ed.), Marcel Decker, pp. 105-163, 1993.

(10) Shay, G.D., "Alkali-Swellable and Alkali-Soluble Thickener Technology," Chapter 25 in *Polymers in Aqueous Media*, ACS Advances in Chemistry Series No. 223, Glass, J.E. (Ed.), pp. 457-493, 1989.

(11) Brookfield KU-1 Viscometer Operating Manual, Brookfield Engineering Laboratories, Inc., Manual No. M/92-240-D294.

(12) Weissenberg, K., *Nature*, Vol. 159, No. 310, 1947.

(13) *Rheology: Theory and Applications*, Eirich, Frederick R. (Ed.), Academic Press Inc., New York, pp. 52-53, 1956.