Rheology of Waterborne Coatings

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Introduction

Waterborne latex coatings were introduced because they are easy to use and lacked the health hazards and noxious odors of their solvent-borne counterparts. Unfortunately, aqueous-borne latex coatings do not possess the same rheological properties of solvent-borne coatings. If not correctly formulated, a latex paint can have inferior flow and leveling properties. They may not give adequate film build, and can be plagued by spattering during application. In order to achieve the equivalent rheology of their solvent-borne counterparts, latex formulations require the addition of rheology modifiers.

Early thickeners or rheological modifiers were derived from starch and casein and were of limited utility. In addition to their biodegradability, they produced poor films and had undesirable flow properties. They were soon replaced with high molecular weight cellulosic thickeners and clays. Cellulosic additives thicken latex systems by polymer chain entanglement. However, their viscosities during application and in drying are not ideal. They are poor in spatter resistance, do not have good flow and leveling properties, and are biodegradable. These inherent disadvantages of cellulosics resulted in the development of associative thickeners for latex coatings beginning in 1980.[1,2] These thickeners have several advantages over cellulosic additives.

Associative Thickeners

The three most popular types of associative thickeners are the styrene-maleic anhydride terpolymers (SMAT), hydrophobically modified alkali-swellable emulsions (HASE), and hydrophobically modified ethoxylated urethanes (HEUR). In each case their use provides advantages and disadvantages over their cellulosic predecessors.[3]

Associative thickeners are low molecular weight water-soluble polymers made of many water-soluble or hydrophilic portions attached to a small number of internal or pendant hydrophobic groups placed either randomly, or in blocks along a polymer backbone and/or as terminal moieties. An associative thickener in an aqueous medium encounters a highly organized water structure. Water molecules are strongly attracted to each other by hydrogen bonding, while the hydrophobes of an associative thickener are only weakly attracted to the water molecules. The strong water hydrogen bonding forces direct the polymer hydrophobes into clusters and thereby minimize the disruption of water structure. Hence, the structuring of water essentially forces the hydrophobic groups together into clusters. Unfavorable entropy does not allow for cluster dissolution. The intramolecular or intermolecular clustering of hydrophobes results in the formation of a pseudo-polymeric-network, in which the hydrophobic clusters are the crosslink junctions.[4,5] The macromolecular hydrophobic moieties may also associate with other hydrophobic surfaces such as the latex particles. This overall as-

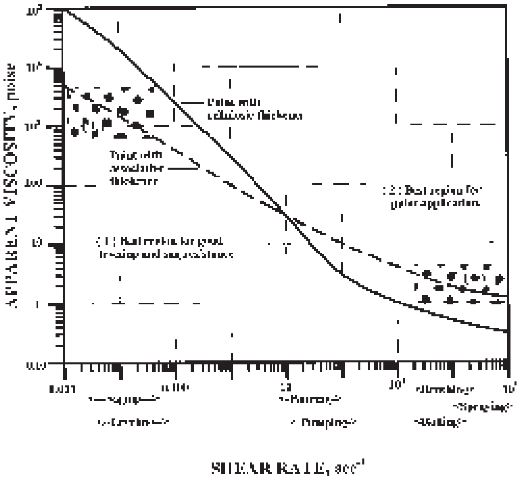

Figure 1—Flow curves of paints with different thickeners.

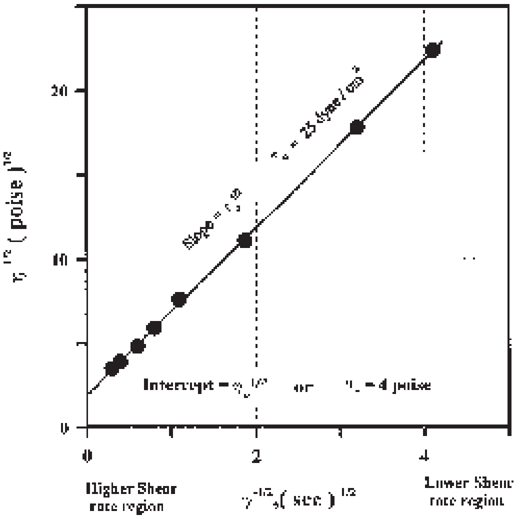

Figure 2—Typical plot of a Casson rheological equation.

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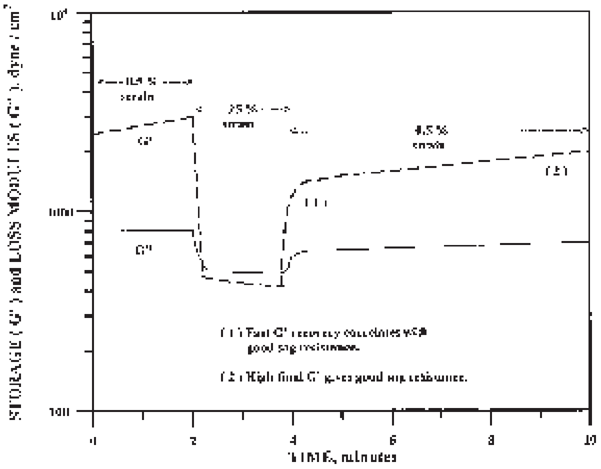

Figure 3—DMA step strain experiment using water-base enamel at a frequency of 10 rad/sec.

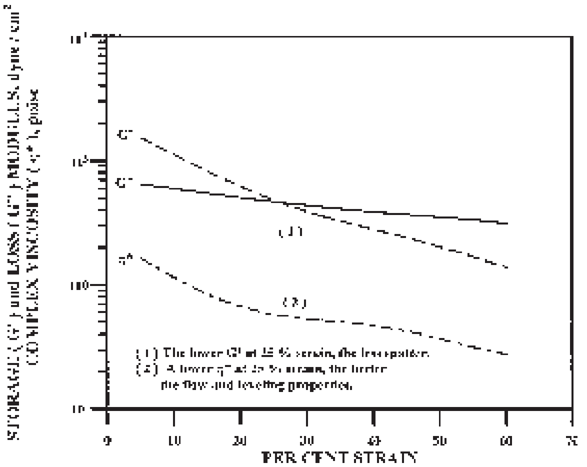

Figure 4—DMA strain sweep experiment at a frequency of 10 rad/sec using a water-base acrylic enamel.

sociation produces an increase in the viscosity of the latex system. The associative thickeners also improve the stability of the system by coating the latex and pigment particles with a protective layer that helps prevent coagulation of the paint during storage.

HYDROPHOBE FORMATION THERMODYNAMICS

The associative strength and duration of hydrophobic clustering are governed by the chemical potential of the hydrophobes and steric factors such as the distance between hydrophobes on the polymer chain. The lower the chemical potential of the hydrophobe the greater the strength of the hydrophobic associations. The equation for the chemical potential, $\Delta\mu$, is:

$$\Delta\mu = 2RT - (V_s + V_p)\,(\delta_s - \delta_p)^2\, X^2 / 2$$

where:

V_s = solvent molar volume
δ_s = solvent solubility parameter
X = hydrophobe volume fraction
T = Kelvin temperature
V_p = hydrophobe molar volume
δ_p = hydrophobe solubility parameter
R = gas law constant

Equation (1) also shows that hydrophobe chemical potential increases (more negative) if the differences in two solubility parameters increases and the molar volume of the hydrophobe increases. If the solubility parameter of the aqueous solvent is adjusted by the addition of cosolvents the strength of the hydrophobic associations can be altered. Thus, the viscosity of the latex system can be controlled.[6]

Other associative-like behaviors such as the enthalpically driven interactions of opposite charges in polyampholytic water soluble copolymers, and hydrogen bonds have also been suggested as the viscosity enhancement mechanism for ion containing associative thickeners.[7]

ADVANTAGES OF ASSOCIATIVE THICKENERS

Associative thickeners are attractive in that higher viscosities at high shear rates lead to good film build per application with little to no roller spatter. Also, their characteristically lower viscosities at lower shear rates is desirable for improved flow and leveling, and high gloss. If the low shear rate viscosity is too high, leveling is compromised and solvent may be trapped to cause poor drying performance. The associative thickeners give better viscosities than cellulosic thickeners in both the low and high shear rate regions. See *Figure* 1. They are also resistant to microbial degradation and are compatible with a variety of latexes.

DISADVANTAGES OF ASSOCIATIVE THICKENERS

Disadvantages of associative thickeners include hydrolytic instability, phase separation, sensitivity to formulation changes, lifting of aged undercoats, and pH dependance. The latter factor is of particular significance in that latex coatings are usually formulated to a pH range of 8-10. This pH assures ionization of carboxyl groups on the latex surface and increases the hydrophilicity of the latex, thereby restricting latex flocculation tendencies with the addition of other formulation ingredients such as pigments and extenders. SMAT and HASE thickeners are particularly pH dependant. Their maximum thickening efficiency is in the pH range of 8-9. The pH range of 8-9 allows essentially complete ionization of their carboxyl groups where the polymer coils are expanded, due to charge-charge repulsions. In this condition, the hydrophobes are exposed and hydrophobic associations are optimized. At other pH values they either are insoluble or possess low thickening efficiencies at lower pH values.

Many latex coatings are pH adjusted with ammonia, a base of high vapor pressure. Thus, evaporation losses can reduce the coating pH, and this produces a loss in the viscosity efficiency of SMAT and/or HASE thickeners. The HEUR thickeners also have another disadvantage. At a pH greater than eight, most urethane functionalities are hydrolytically unstable leading to bond cleavage

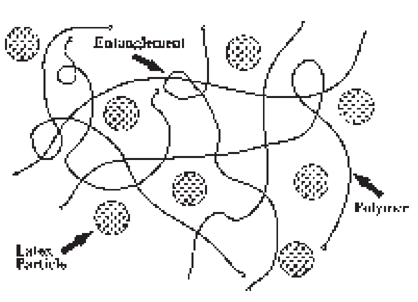

Figure 5—Polymer chain entanglement.

that lowers the molecular weight and results in a loss of thickening efficiency.[8]

RHEOLOGY OF ASSOCIATIVE THICKENERS

There are two main rheological criteria for evaluating thickener efficiency. First, a thickener must have low shear viscosities which give an aesthetically pleasing in-can image of the coating, non-dripping properties, good flow and leveling, and minimum sagging tendencies. An efficient thickener must also provide adequate coating viscosity at the application shear rate so that high build in film thickness will occur and brush or roller drag will be minimized.[9] Finally, the coating extensional viscosity and elasticity must be low so that spattering and stringing will be absent.

Thickening efficiencies are determined using laboratory rheometers. The flow conditions studied in the laboratory must simulate the process conditions during the coating application and film drying. The instruments usually employed for this purpose are the Brookfield and Stormer viscometers, and an ICI cone and plate rheometer.

The Brookfield and Stormer viscometers are used to study low shear properties such as in-can thixotropy, dripping, flow and leveling, and running or sagging tendencies. The Stormer and low shear Brookfield viscosities correlate with brush pickup properties and flow from the can characteristics. These measurements often predict film leveling and sagging performance.

The ICI rheometer which operates at a high shear rate (10^4 sec^{-1}) allows prediction of fluid properties at shear rates similar to coating application conditions. ICI fluid viscosities of 1 to 2 poise usually indicate that excessive drag would be absent during the coating application.

Brookfield viscometers are used to study the low shear behavior of latex systems. These instruments can operate at low shear rates from about 0.1 to 100 sec^{-1}. These lower shear rates are comparable to that present during film leveling.

$$\sqrt{\eta} = \sqrt{\eta_\infty} + \frac{\sqrt{\tau_0}}{\sqrt{\gamma}}$$

The Casson equation is used with the Brookfield low shear measurements to predict coating viscosity at high shear rates.

The Casson equation shows that a plot of $\sqrt{\eta}$ versus $1/\sqrt{\gamma}$ data should be linear. The high shear viscosity, η_∞, and yield stress, τ_o, can be determined from the intercept and slope of the straight line fitted to the data[10] (see *Figure* 2). Due to the shear thinning nature of most coatings, nonlinear behavior is found at higher shear rates. The parameters, η_∞ and τ_o, should always be determined from the low shear region of the plot.[11]

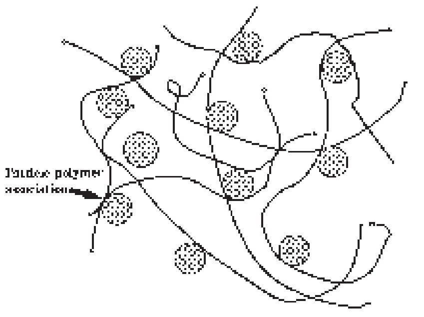

Figure 6—Polymer bridging between latex particles.

The calculated high shear viscosity from the Casson equation is comparable to the ICI high shear viscosities. The yield stress value is used to ascertain the sagging tendencies of an applied coating. Yield stress values measured before and after high shear mixing are important. To prevent settling during storage, a latex coating should have before high shear mixing yield stress and viscosity values greater than 10 dynes/cm^2 and 500 poise, respectively. However, a latex coating must also have a yield value less than 2.5 dynes/cm^2 and a lower viscosity immediately after high shear mixing to insure good flow and leveling. After high shear mixing, the yield stress value and viscosity must quickly increase over a short time period to prevent sagging.[12,13,14]

DYNAMIC MECHANICAL ANALYSIS OF LATEX COATINGS

Dynamic mechanical analysis (DMA) can also be used to determine the flow properties of a latex coating. In DMA, the coating is forced to undergo a harmonic strain at a given frequency, ω. The resulting stress on the coating can be divided into an elastic component, the storage modulus (G′), and a viscous component, the loss modulus (G″).

Viscoelastic parameters determined by DMA can be used to predict spatter resistance, sagging, and flow and leveling of thickened latex systems.[15] Spatter resistance is predicted by measuring the elastic modulus G′ at high strains. If G′ is reasonably low, latex spattering is minimum. Flow and leveling can also be predicted by measuring the complex viscosity, η*, versus strain. The complex viscosity is determined from the storage and loss modulus. The complex viscosity at frequency ω is defined as

$$\eta^* = \sqrt{\left(\frac{G'}{\omega}\right)^2 + \left(\frac{G''}{\omega}\right)^2}$$

Systems with lower η* have better flow and leveling properties. See *Figures* 3 and 4.[15]

PROPOSED THICKENING MECHANISMS IN LATEX SYSTEMS

The associative polymer mechanism, which is active to thicken latex coatings, is a subject of debate. One proposed mechanism of thickening involves the formation of hydrophobic clusters, which increases the viscosity of the system. Another suggests that the thickening mechanism involves the association of the latex particles with the hydrophobes of the associative polymers thereby producing a pseudo polymeric structure of very high molecular weight, increased hydrodynamic volume, and system viscosity. Both mechanisms in addition to chain entanglement may be active. Also, the mechanism that dominates may depend upon the coating formulation (latex, pigment, co-solvent, surfactant type, and concentration).

CHAIN ENTANGLEMENT

The chain entanglement theory applies to water-soluble polymers of high molecular weight such as the cellulosic thickeners. Polymers of high molecular weight such as hydroxyethyl cellulose possess a large hydrodynamic volume in aqueous systems. When these polymers are above their critical overlap concentration and exceed a critical molecular weight, entanglement of polymer coils occurs causing a viscosity enhancement of the latex system. There is no polymer interaction with the latex par-

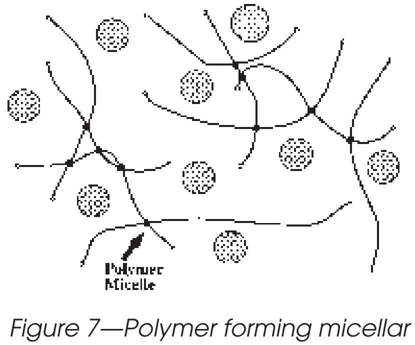

Figure 7—Polymer forming micellar bridges.

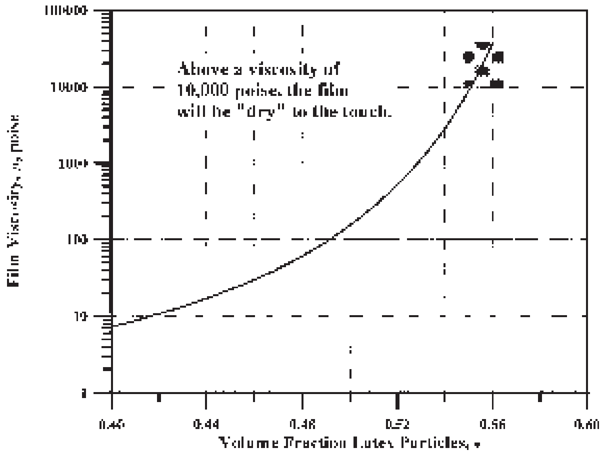

Figure 8—Film viscosity during curing.

ticles. When placed in a flow field there is a tendency for entangled polymers to orient with the flow field causing them to disentangle and this produces a decrease in the viscosity of the coating. Excessive shear thinning results in thin paint films having poor hiding characteristics.

In addition, these thickeners of high polymer molecular weight impart a large degree of elasticity to the coating. The polymer molecules can store elastic energy when they are elongated during a coating application. With removal of the force field after coating application, there is a fast recovery of the elongated polymers back to their unperturbed state. This release of stored energy causes the coating to have poor flow and leveling properties and also spatter[6] (see *Figure* 5). Thus, latexes with higher elongational viscosities will spatter more than coatings with lower extensional viscosities.[16]

PARTICLE BRIDGING

Water-soluble polymers which are considered to thicken by a particle bridging mechanism are lower in molecular weight than the chain entanglement thickeners. This theory of association maintains that the hydrophobes of the low molecular weight polymer molecules are adsorbed onto the latex surfaces. The water-soluble polymer segments are free to extend into the aqueous medium. Thus, it is assumed that the polymer hydrophobes can effectively compete with surfactants and colloidal stabilizers for the latex surface adsorption sites. Polymer adsorption leads to an extensive network of latex particles loosely coupled together by low molecular weight polymers (see *Figure* 6). The coating would have a high viscosity at low shear conditions because of the network structure. However, in a shear field, the hydrophobes are desorbed from the latex surface. This destroys the network and reduces the coating viscosity during the application. This mechanism produces shear thinning, but not the extent experienced by the high molecular weight thickeners that produce enhanced fluid viscosity by polymer entanglement. After coating application and removal of the shear field, there is a slow re-adsorption of the polymer hydrophobes onto the surfaces of the latex particles. This leads to improved flow and leveling for latex systems thickened with associative polymers.[17] Because the network structure degenerates in the shear field produced by the application process, very little elastic energy is stored within the coating during application. Thus, the latex has less spatter.

MICELLAR BRIDGING

The micellar bridging mechanism requires the formation of hydrophobic clusters which causes a network of loosely coupled low molecular weight polymers to form within the system. In contrast to the particle bridging theory, hydrophobic associations with the latex particles are not necessary to form a viscous coating (see *Figure* 7). In a shear field, the hydrophobic clusters are broken up and shear thinning occurs. However, since the polymers of associative thickeners are lower in molecular weight and are more flexible than the polymers used by chain entanglement thickeners, they do not readily orient or elongate with the shear field and thus have larger high shear viscosities. This leads to higher film builds and better hiding. When the shear field is removed, recovery of the hydrophobic clusters is not instantaneous. This causes the coating to be less elastic which produces better spatter resistance and good flow and leveling properties.

RHEOLOGY DURING LATEX COATING CURING

The Mooney rheological equation can be used to describe the viscous properties of a latex dispersion during the process of film formation.[18] The Mooney equation shows that the low shear viscosity of the system, is the result of magnifying the viscosity of the external fluid phase, η_e, by an exponential. For latex systems the external fluid is composed of water, co-solvents, surfactants, and other fluid additives. The value for η_e is about 0.5 poise. The value of the exponential term is dependent upon the volume fraction of solid particles making up the internal phase, ϕ, and constants K_1 and K_2. These constants are related to the shape and packing properties of the solid latex particles. For latex particles which are spherical, K_1, the shape constant, equals 2.5. The packing constant, K_2, is the volume fraction of internal phase present when the solid latex particles are packed in close contact. The K_2 value for spheres in a random, close-packed state is about 0.64.

$$\eta = \eta_e \ \mathrm{EXP}\frac{K_1K_2\phi}{K_2 - \phi}$$

Figure 8, a plot of the Mooney equation for a typical latex, shows the rapid increase in coating viscosity that occurs as solvent evaporation from a film increases the volume fraction of latex particles. As the latex particles approach one another, capillary forces overcome particle-particle repulsion forces and coalescence into a solid film can occur. Usually a less volatile solvent is still present during the final stages of evaporation which plasticizes the polymer latex and thus assists in film coalescence. After coalescence is completed, this solvent slowly diffuses through the film to the surface and evaporates. The film will be “dry to the touch” when the system viscosity reaches 10^4 poise. After complete film curing, the viscosity exceeds 10^8 poise.

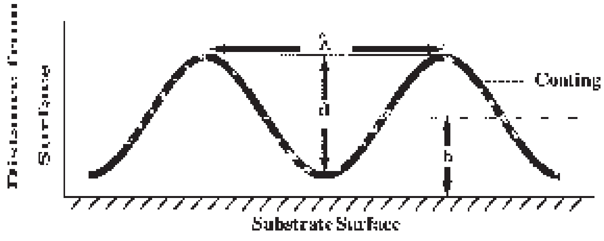

Figure 9—Cross-section of coated substrate with brush mark pattern.

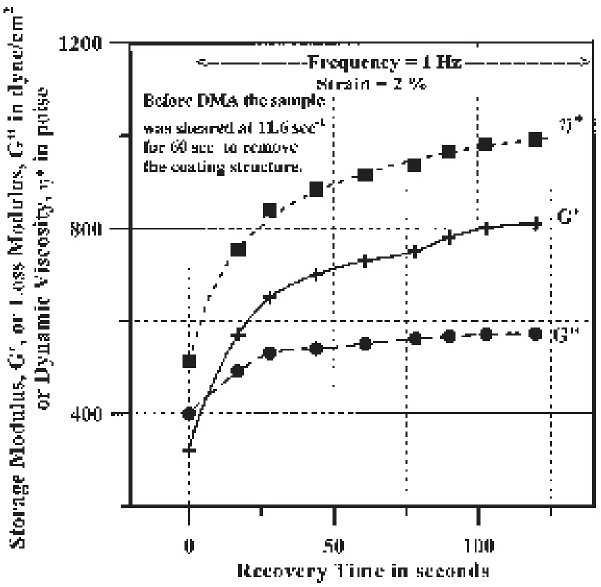

Figure 10—DMA analysis showing coating structure reformation after shear.

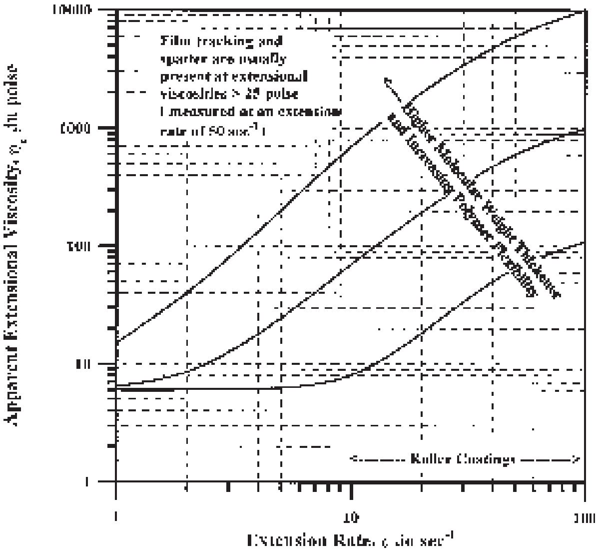

Figure 11—Typical extensional viscosity behavior of polymer thickened coatings.

RHEOLOGY DURING LEVELING

The leveling of brush marks can be considered as a process where the drive toward equilibrium to a smooth surface is controlled by two opposing forces. Film leveling or flow is driven by surface tension forces which are resisted by fluid viscous forces. The leveling stress, τ, developed for a coating having a surface tension of y can be approximated by[19]

$$\tau = 4\,\pi^3\, y\, h\, d\, /\, \lambda^3 \quad \text{or} \quad d = \frac{\tau\, \lambda^3}{4\,\pi^3\, y\, h}$$

Where h is the average wet coating thickness, d is the brush mark depth and, λ is the brush mark wavelength (see *Figure* 9).

During leveling, y, λ, and h remain almost constant therefore, the leveling stress decreases as the brush mark depth decreases. The amount of coating flow which decreases brush mark depth during the leveling process depends upon the rheological properties of the coating. Leveling will cease when the leveling stress, τ, becomes equal to or less than the coating's yield stress, τ_o. Thus, the final brush mark depth can be found from equation (5) when we let τ equal to τ_o.

For example, latex coatings are usually applied at a wet thickness of 0.01 cm (4 mils) and typically have an after high shear mixing yield stress of 2 dyne/cm^2. The coating surface tension is about 25 dyne/cm. The wavelength of a brush mark varies but is about 0.1 cm. Using these application conditions, the relationship gives a final brush mark depth of about 6×10^{-5} cm (0.03 mils).

After film application, the coating viscosity must remain low long enough for leveling but then increase in viscosity with time to prevent film sagging. Otherwise, the flow rates for leveling must be faster than the viscosity increase due to the thixotropic nature of the coating. However, after leveling the viscosity must increase rapidly to prevent film sag. The total time for leveling varies with coating properties and is usually between 30 and 300 sec.[20]

DMA has been used to study the thixotropic or recovery properties experienced by a high solids enamel during leveling.[21] The enamel sample was first subjected to continuous strain to simulate the removal of rheological structure during a coating application. Thereafter, the increase in the storage and loss moduli was used to indicate the rate at which the structure reforms to prevent film sagging. *Figure* 10 shows that the dynamic viscosity rate of increase diminishes as the structure reforms. After about 300 sec the dynamic viscosity stabilizes to about 1200 poise. This suggests that all structure reformation is complete after this time period.

EXTENSIONAL VISCOSITY

Newton, the father of rheology, defined the shear rate, γ, as the change in fluid velocity with respect to the direction which is perpendicular to the fluid velocity. The shear stress, τ, is determined from the product of the fluid's apparent shear viscosity, η, and the shear rate, i.e., $\tau = \eta\ \gamma$. As previously explained, paints are shear thinning, i.e., the shear viscosity decreases with increasing shear rates.

In contrast, the extensional strain rate, ε, is the change in fluid velocity with respect to the direction parallel to the fluid velocity. The extensional stress, τ_e, is determined from the product of the fluid's extensional viscosity, η_e , and the extensional strain rate, i.e., $\tau_e = \eta_e\ \varepsilon$.

Measurement of the extensional viscosity is difficult because a constant extensional strain rate cannot be easily maintained on a fluid. Trouton[22] showed that at very low extension rates the extensional viscosity is three times the apparent shear viscosity measured at very low or "zero" shear rates. Most coatings show Troutonian behavior at low extensional strain rates but are also tension

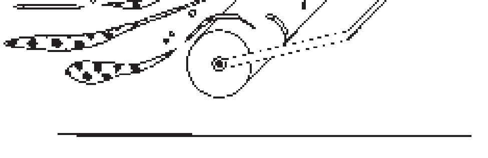

Figure 12—Splatter during roller application.

Table 1—Rheology Required for Good Thin Film Formation

Coating Process Step	Shear Rate (sec^{-1})	Viscosity (poise)	Yield Stress ($dyne/cm^2$)
Storage	0.1	>500	>10
Transfer to brush with dripless character	20	>25	>10
Substrate transfer with good film build-up and without excessive brush drag	10,000	1 to 3	<2.5
Drying with good leveling and minimum sagging	1.0	50 to 100	<2.5

stiffening at higher extensional strain rates. Fluids are tension stiffening when they have extensional viscosities that increase rapidly with increasing extensional strain rates. The increase in the extensional viscosity of coatings thickened with polymers is more rapid with increasing polymer molecular weight and macromolecular conformational flexibility (see *Figure* 11). Coatings with high extensional viscosities give spatter problems during application.[23]

When a paint has a high extensional viscosity then thin fibers or slender strings may form and lengthen during application. These elastic fibers eventually break. After breakage the fibers snap back onto both the substrate and applicator. The release of the energy stored within the elongated fibers results in the formation of small airborne paint droplets which produce splatter (see *Figure* 12). This same energy storage and release mechanism can also create coating tracks or surface patterns on the substrate.

Paints which use entangled high molecular weight polymers to increase viscosity usually have high extensional viscosities which give spatter. High molecular weight polymers maintain a high degree of entanglement when elongated. These entanglements store the elastic energy needed to promote spatter. Entanglement decreases with decreasing molecular weight.

In contrast, associative thickeners do not have high extensional viscosities because the network structures formed by polymer-polymer or polymer-latex associations are destroyed when the network is elongated. Elastic energy cannot be stored and released during the coating application and thus spatter and surface defects are minimized.

Summary

The rheology of a latex paint must be controlled to produce an acceptable coating. Conditions vary as a paint is sequentially taken from storage, applied to a substrate and then cured in place. As shown by *Table* 1, desirable films are produced only when paint viscosities and yield points are controlled at each process step. Thus, an understanding and control of paint rheology are essential if high quality coatings are to be produced from latex paints.

REFERENCES

(1) Calbo, L. J., *Handbook of Coatings Additives*, Chap. 2, Marcel Dekker, New York, 1986.

(2) Oil and Colour Chemist's Association of Australia, *Surface Coatings, Vol. 1*, Chap. 23, Tafe Books, Randwick, Australia, 1983.

(3) Schwab F. G. and Glass J. E., *ACS Advances in Chemistry, Ser. 213*, 369 (1986).

(4) Sau A. C. and Landoll, L. M., *ACS Advances in Chemistry, Ser. 223*, 344 (1989).

(5) Lochhead, R. Y., *Coatings Technology Shortcourse Notes*, 18 th Waterborne and High Solids Coatings Symposium, New Orleans, LA (1991).

(6) Hoy, K.L., U. S. Patent 4,426,485 (1984).

(7) McCormick, C. L., Bock, J., and Schulz D.N., *Encyclopedia of Polymer Science, 2nd Ed.*, Vol. 17, 730, 1989.

(8) Shay, G. D., *ACS Advances in Chemistry, Ser. 223*, Chap. 25, 457 (1989).

(9) Glass, J. E., *4th International Conference in Coatings Sci. and Tech.*, 83, 1980.

(10) Cutrone, L., "Use of the Brookfield Viscometer to Predict Pheological Performance of Coatings," JOURNAL OF COATINGS TECHNOLOGY, *56*, No. 708, 59 (1984).

(11) Sato, T., "Rheology of Suspensions," JOURNAL OF COATINGS TECHNOLOGY, *67*, No. 847, 69 (1995).

(12) Pierce, P.E.,"Rheology of Coatings," JOURNAL OF PAINT TECHNOLOGY, *41*, No. 533, 383 (1969).

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

(14) Karunasena A., Brown, R. G., and Glass J. E., *ACS Advances in Chemistry, Ser. 223*, Chap. 26, 495, 1989.

(15) Tso, S.C. and Rohn, C., *Proc. 15th Waterborne and High Solids Coatings Sym.*, New Orleans, LA, 244, 1988.

(16) Glass, J. E., "Dynamics of Roll Spatter and Tracking-Part III: Importance of Extensional Viscosities; Part IV: Importance of G* Recovery and N1 in Tracking," JOURNAL OF COATINGS TECHNOLOGY, *50*, No. 641, 56 (1978).

(17) Sperry P. R., Thibeault, J. C. and Kostansek, E. C., *Adv. Org. Coatings Sci. Tech., Ser. 9*, 1, 1985.

(18) Wicks, Z. W., "Film Formation," *Federation Series on Coatings Technology*, Philadelphia, PA, 12, 1986.

(19) Jackman, M., *Rheology Pro Files, Vol 12, No. 1*, Haake Buchler Instruments, Saddle Brook, NJ, 3, 1985.

(20) Schoff, C. K., "Rheology," Federation Series on Coatings Technology, Blue Bell, PA, 34, 1991.

(21) Smith, A., Reichert, W.W. and Nae, H., JOURNAL OF COATINGS TECHNOLOGY, *62*, No. 784, 45 (1990).

(22) Trouton, F. T., *Phil. Mag.*, *21*, 426 (1906).

(23) Glass, J. E., *Adv. Org. Coatings Sci. Tech., Ser. 2*, 83 (1978).