Rheology of coating colors and their runnability on a cylindrical laboratory coater

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ABSTRACT

We present results of our ongoing study on the rheology of coating colors. For this study, we chose simple coating colors made up of kaolin and latex and report results on the transient viscosity at low shear rate and small-amplitude oscillatory data obtained using a controlled-strain rheometer. The rheological properties are compared with runnability results on a Cylindrical Laboratory Coater. We report a surprisingly good correlation between low-deformation transient rheological measurements and runnability. Although very large deformation rates (≈10^6 s^{-1}) are encountered in the coating process, the contact time for the flow under the blade is extremely small (≈10^{-5} s). Thus, low-deformation rheological characterization is believed to be significant in relation to coating.

Application: *Model studies suggest that coating runnability can be predicted by measuring shear rheology at low deformation.*

COATING COLORS HAVE COMPLEX rheological characteristics *(1-3)*. The complex rheology reflects the presence of solid particles in high-volume concentrations as well as the interactions between pigment particles, dispersants, binders, and other additives. Control of the rheological properties and the dewatering rate of coating colors is essential to achieve satisfactory runnability when coating at high speed *(2, 4)*. Moreover, coating rheology affects the quality of coated and printed papers *(5, 6)*.

The viscoelastic properties of coating colors affect runnability during blade coating *(7, 8)*. Yield stress has also been postulated as a possible controlling parameter *(9)*. It has been shown that for typical commercial trailing-blade coaters running at 600 m/min with a blade gap of 10 µm, the average deformation rate at the blade tip is about 10^6 s^{-1}, while the time spent by a fluid element under the blade is about 10^{-5} s *(10)*.

Steady-state rheological measurements at comparably high shear rates have shown that the elastic component becomes negligible compared with the viscous response, i.e., the colors are virtually inelastic at the higher shear rates *(1, 11)*. However, low-shear measurements remain important to understand the coating behavior in the overall process.

Triantafillopoulos *(11)* has shown that low-shear viscosity and yield stress are associated with short-dwell streaks. He explained how these parameters contribute to hydrodynamic instability phenomena in the flow before the passage under the blade and pointed out their effect on the time needed for particles to align parallel to the streamlines. Engström and Rigdahl *(3)* have shown that low-shear rheometry is a powerful tool for characterizing aggregation in coating colors, which affects the whole process. They investigated the effects of binder and CMC (carboxymethyl cellulose) concentration for kaolin and calcium carbonate suspensions. Davis *(12)* determined the yield stress of CMC–latex colors using the Casson equation and related the yield stress to the adsorption of CMC (through hydrogen bonding) on kaolin particles. Lepoutre *et al.* *(13)* showed that the addition of electrolytes increases the suspension viscosity, the yield-stress value, and the shear-thinning character, while Lepoutre and Lord *(6)* demonstrated that the porosity of dried colors increases with ionic content. This confirms the increasing role of aggregation in kaolin suspensions with ionic content, but more importantly, it suggests that low-shear rheometry may yield very useful information on the phenomena associated with aggregation and their contribution to final coating structure. Measurements at high shear rates will not reveal the pertinent information, since the yield stress (particle–particle interactions) becomes negligible compared with the viscous forces. Moreover, the elastic response of the fluid is too rapid to be measured.

Several investigators have tried to correlate blade-coater performances and the rheological behavior of coating colors *(9, 14–21)*. Purkayastha and Oja *(9)* observed some correlation between dynamic rheological measurements and runnability on a Cylindrical Laboratory Coater (CLC). Engström *(15)* reported no correlation between bleeding and dilatancy (shear-thickening) of coating colors. Ramthun *et al.* *(16)* developed a high-shear rheometer by modifying a high-pressure homogenizer with a shearing nozzle, and they were able to measure the rheological characteristics at shear rates of 10^5–10^7 s^{-1} in a nozzle-type geometry at a short dwell time. Vidal *et al.* *(17)* modified the blade of a blade coater to obtain an *in situ* rheometer that they claimed allowed them to make rheological measurements in a "real" environment. Tsuji and Sasagawa *(18)* developed a "slit die rheometer" that can accurately measure the steady-high-shear rheological properties and the excess pressure drop at the entrance of the slit. This setup was developed to simulate the flow behavior below the blade. Grankvist *et al.* *(19)* observed that coating colors with lower values for high-shear viscosity (as measured using a capillary rheometer) usually gave better runnability. Roper and Attal *(20)* also gathered data using a capillary rheometer. With a suitable rheological model and computational method, they were able to predict the blade pressure reasonably well. Recently, Wilson and Greenblatt *(21)* obtained rheological data of coating colors at high shear rates (2×10^3 to 2.75×10^5 s^{-1}). By making suitable end corrections, they concluded that the extensional viscosity is an important factor affecting the coat weight. Of course, other factors such as water-retention capacity of the coating color *(2, 4, 19)* and the basestock properties are also important.

Component	Trade name, manufacturer	Form
U.S. coating kaolin		
Standard No. 2	HT™, Engelhard	70 wt.% slurry
Standard delaminated	Nuclay™, Engelhard	69 wt.% slurry
SB carboxylated latex	Gen-Flo™ 5086, Gencorp	50 wt.% emulsion
High-viscosity CMC	CMC-7H, Aqualon	dry powder

I. Trade names of various components in the coating colors

Kaolin type in coating color	Solids content, wt.%	pH	Brookfield viscosity, mPa·s	Hercules end point, N·m
Delaminated	66	8.0	1000	0.44
	64	8.0	1000	0.36
	62	8.0	1000	0.24
No. 2	67	8.0	1000	0.38
	63	8.0	1000	0.19

II. Key properties of the coating colors

EXPERIMENTAL

The coating color formulations used in this work consisted of 100 parts (by weight) of pigment and 11 parts (by weight) of SB (styrene–butadiene) carboxylated latex. The pigments were a standard No. 2 U.S. kaolin (available as a 70 wt.% slurry) and a standard delaminated US kaolin (available as a 69 wt.% slurry). The pH of the color was adjusted to 8.0 by adding a 10 wt.% caustic solution. The fraction of solids was adjusted by adding water, if necessary. The Brookfield viscosity of each color was then adjusted to 1000 mPa·s (1000 cP) at 100 rpm (No. 4 spindle) by adding a "high viscosity" type CMC as dry powder. The trade names of the various components are listed in **Table I**.

Coating colors were mixed for a reasonable length of time (usually 15–20 min) to ensure a homogeneous suspension without any lumps. The coating colors containing the standard No. 2 kaolin were made down at total solids of 67 wt.% and 63 wt.%, and the coating colors containing the standard delaminated kaolin were made down at 66 wt.%, 64 wt.%, and 62 wt.% solids. These simple coating colors were used as model suspensions.

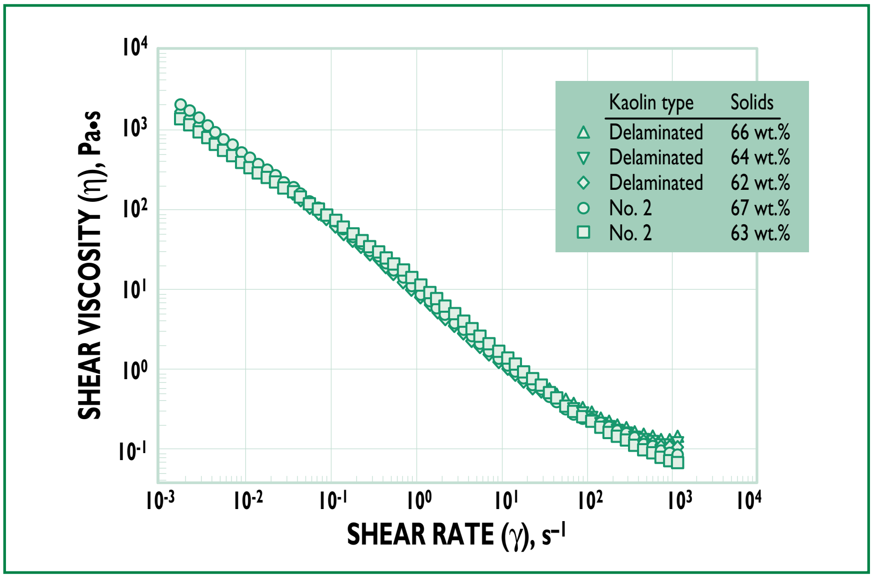
The colors made with only delaminated kaolin at high solids content were prepared mainly to obtain a low critical speed on the cylindrical laboratory coater (CLC) and to highlight the low-shear contribution of yield stress and stress growth function on runnability. The two colors containing No. 2 kaolin were made down for reference. The higher solids level was chosen so as to observe the onset of runnability problems (defined later) on the CLC. The lower solids content was chosen such that its Hercules end point was appreciably different from that of the previous formulations, while still ensuring that it showed a critical coating speed on the CLC. Key properties of the five coating colors are presented in **Table II**.

The basestock chosen was an offset-type paper with a basis weight of 37–44 g/m² (25–30 lb/3300 ft²). The rheology of the coating colors was studied using a strain-controlled Bohlin VOR rheometer (Bohlin Instruments, Inc., Cranbury, NJ). All measurements were conducted at a constant temperature of 25°C using a bob-and-cup geometry (25-mm diam. and 1-mm gap). Steady-shear viscosity, transient viscosity (imposed constant shear rate), as well as data for strain and frequency sweeps in small-amplitude oscillatory-shear mode were obtained. Static dewatering rates were measured in a AA-GWR (Kaltec Scientific, Inc., Novi, MI) apparatus at 1 atm gauge pressure for 120 s and five sheets of basestock.

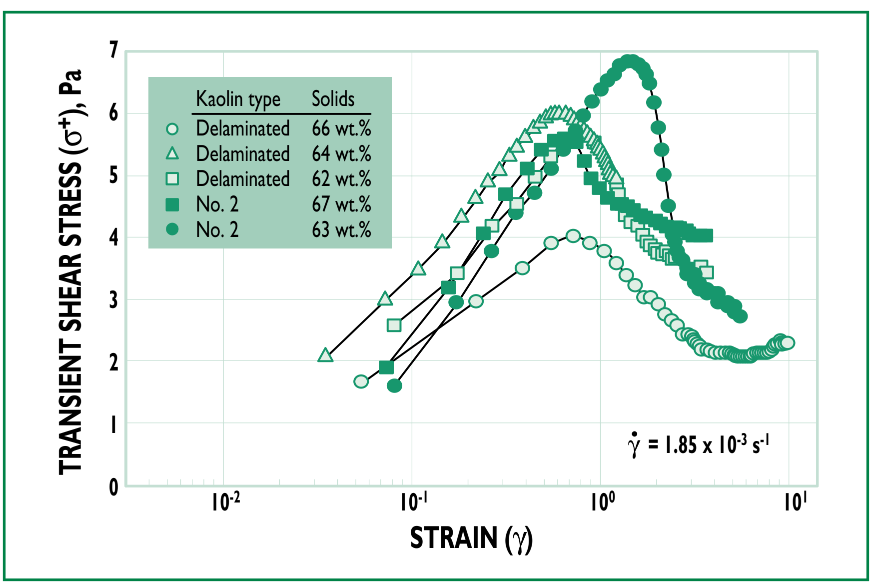
Coating studies were carried out on a Cylindrical Laboratory Coater (Sensor & Simulation Products, Tacoma, WA) under identical conditions for each coating color: a constant coat weight of approximately 7.4 ± 0.75 g/m² (5 ± 0.5 lb/3300 ft²), and steps of 150 m/min (500 ft/min). The blade position was adjusted so as to obtain the target coat weight, starting at the lowest coating speed, which was 450 m/min (1500 ft/min) for the colors with the delaminated kaolin, and 600 m/min (2000 ft/min) for the color with the standard No. 2 kaolin.

For the purposes of this study, we define runnability as the critical coating speed on the CLC at which visible coating bands or wet streaks *(22)* begin to appear. For this study, we did not evaluate the influence of basestock properties on runnability.

We wish to state the limitations and the scope of this study. The coating colors were simple kaolin–



1. Shear viscosity (η) as a function of shear rate ($\dot{\gamma}$) for the five coating colors

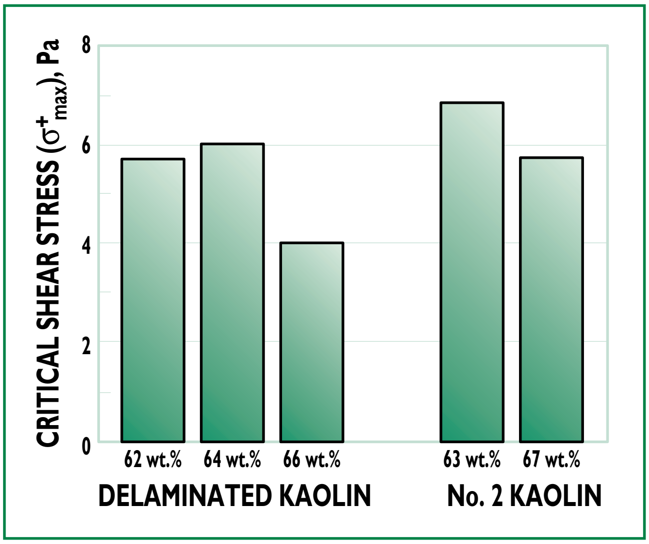


2. Transient shear stress (σ^+) as a function of strain (γ) at a constant shear rate ($\dot{\gamma}$ = 1.85 x 10^{-3} s^{-1}) for the five coating colors

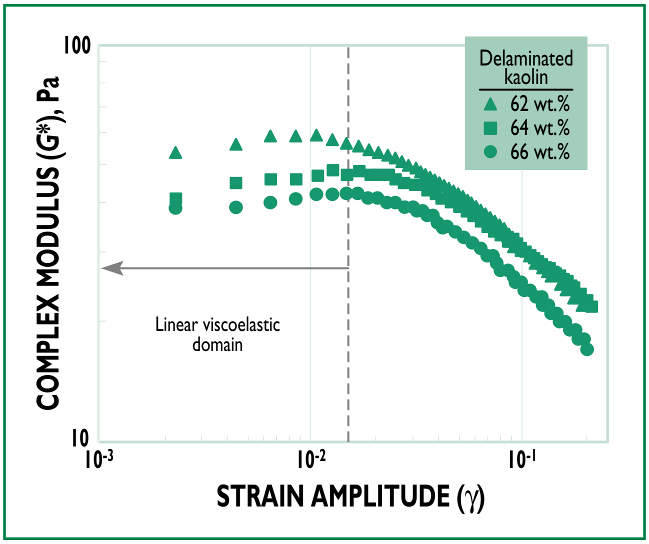
latex–CMC formulations. These may or may not reflect the rheological behavior of other formulations, viz., those containing starch or associative thickeners. Because of the difficulties in controlled experiments of coating colors containing starch, we had to settle on doing our work with these simple formulations. However, we plan on working with such formulations in the future. The other limitation of this study is the use of a pond-type CLC, which may or may not correlate with the trailing-blade coaters, the most popular commercial coaters. On a CLC, it is rather easy to control the coating speed. In the industry, "coater runnability" has come to mean an umbrella of defects *(22)* that may or may not have an origin in the rheological behavior of the coating color. In our opinion, the minimum coating speed at which defects start to appear would be a realistic effect manifesting itself due to the rheological behavior of coating colors.

RESULTS AND DISCUSSION

Because of the high particle content in coating colors, the particle–particle interactions result in a solid-type rheological behavior (the material can be deformed but will not flow) at low deformation (or strain). Moreover, the rheological behavior of coating colors is strongly dependent on strain and on the degree of particle dispersion. The studied coating colors did not exhibit low-shear plateau (or Newtonian behavior), as is observed for homogeneous solutions or dilute suspensions in simple steady-shear experiments. As illustrated in **Fig. 1**, the viscosity is unbounded at lower shear rates, i.e., viscosity approaches infinity as the shear rate appraches zero, and this is an indication of solid-type behavior. The stress required to break the particle arrangement and to cause the system to flow is referred to as an apparent yield stress. For highly concentrated suspensions such as coating colors, the solids generally are not evenly distributed because of the presence of aggregates and flocs. Such structures can change with time, and other structural arrangements can develop under applied stresses. (Coating colors are usually thixotropic, i.e., the viscosity decreases with time at a constant shear rate.) In most industrial operations, the viscosity of the coating color is adjusted at a given shear rate using viscosity modifiers, to take care of constraints such as pumping operations. The drop in viscosity due to the use of a lower solid content is adjusted by adding suitable viscosity modifiers such as CMC. The viscosity modifiers act as water-retention agents and are believed to stabilize the flow in the dwell by increasing the particle–particle interactions *(11)*. This is particularly significant for kaolin suspensions when CMC is added. In this study, all coating colors were adjusted to a Brookfield viscosity of 1000 mPa·s (1000 cP) at 100 rpm (No. 4 spindle) by adding CMC as needed. The various particle–particle and particle–polymer



3. Critical (maximum) shear stress from Fig. 2 for the five coating colors



4. Complex modulus (G) as a function of strain amplitude (γ^0) for coating colors containing standard delaminated kaolin at frequency (ω) of 1.0 Hz*

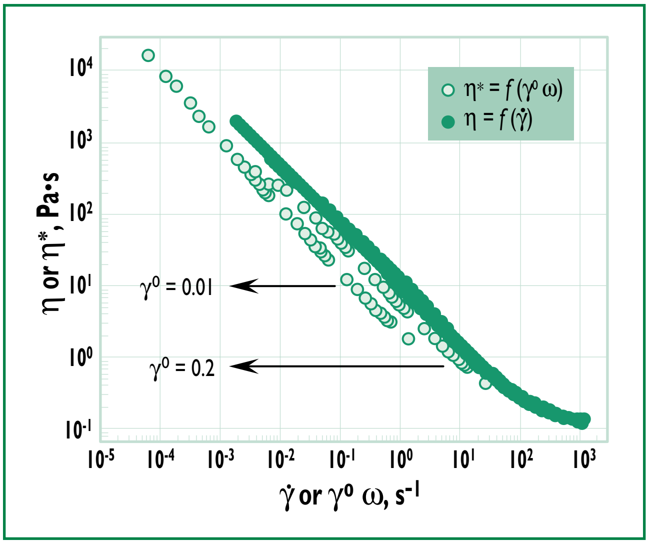
interactions have a significant effect on the electrostatic stabilization of the colloidal kaolin particles, thereby affecting the macroscopic parameters such as rheology, water retention, and runnability *(2, 6, 12)*.

Figure 1 compares the steady-shear viscosity as a function of shear rate for the five coating colors. To avoid problems from structure changes with time (thixotropic effects), the viscosity measurements were made from high to low shear rates. An equilibrium time of 10 s was imposed for each measurement, and the reported values are time-integrated values for 10 s. (For measurements done from low to high shear rates, an equilibrium time as long as 1000 s would have been required to obtain a steady-state value at the lower shear rates, and the transient viscosity value could vary in that time interval by a factor of ten.) All five curves in Fig. 1 approximately superimpose except at the highest shear rates. This is not surprising, since the viscosity–shear-rate dependence is dictated by the geometry and concentration of the particles, and the Brookfield viscosity for each coating color had been adjusted to the same value at a given shear rate. Thus, steady-shear viscosity vs. shear rate in the range from 10^{-3} s^{-1} to 10^{3} s^{-1} can hardly be used to discriminate differences in runnability between the coating colors used in this study.

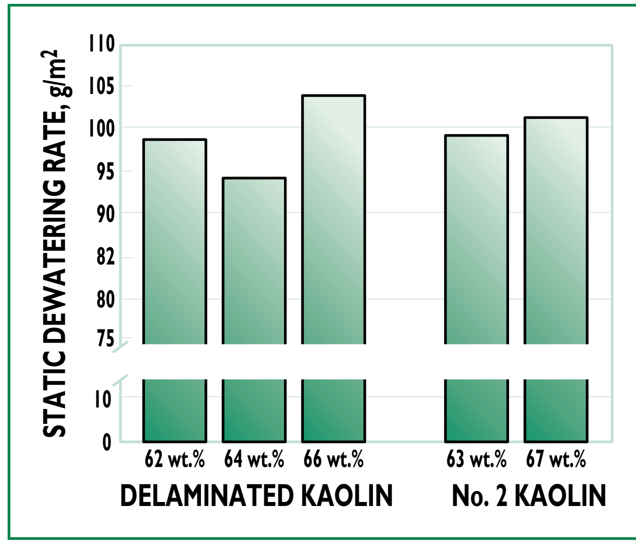
Figure 2 presents the transient viscosity of the coating colors in a startup experiment. A constant shear rate (1.85 x 10^{-3} s^{-1}) was applied to each coating color after equilibrium (without prior important deformation). The measured shear stress is reported as a function of the calculated strain (equal to the product of shear rate and time). For each suspension, a peak in the stress response is observed at a strain of about 1 unit (or 100%). Similar behavior was observed at higher shear rates, but data collection was restricted by the rheometer's acquisition system. For example, at a shear rate of 1 s^{-1}, the critical strain was reached in 1 s. The critical strain observed in Fig. 2 represents the limit between the viscoelastic solidlike behavior and the viscoelastic liquidlike behavior. The maximum stress can be interpreted as an "energy barrier" that must be overcome before the suspension can start to flow. This result is very important for the coating process. If deformation rates in the coating process are very high (10^6 s^{-1}), the deformation for the flow under the blade (product of deformation rate and time for the coating color to pass under the blade) is very low, about 10. Thus such low strain results, obtained at low shear rates, are essential to understand the coating process.

The maximum stresses (critical stresses) reached in the startup experiments of Fig. 2 are replotted as a bar chart in **Fig. 3**. For the colors containing No. 2 kaolin, the critical stress decreased with increasing solids content. This is probably related to the effect of the high-molecular-weight CMC concentration, which was increased as we lowered the solids content to maintain a constant Brookfield viscosity. Obviously, for a given suspension, the elastic modulus and the yield stress increase with increasing CMC concentration. For the delaminated kaolin colors, the critical stress was highest at 64 wt.%, while critical stress was much lower at 66 wt.%. We have no explanation for this trend. Our tentative assumption is that it reflects the compensating effects of lowering the solids content and increasing the CMC concentration. Further measurements of the interactions using other techniques will be needed to clarify this finding.

Small-amplitude oscillatory shear data presented in **Figs. 4 and 5** are an indication of the level of interactions between components of the suspen-



5. Shear viscosity (η) as a function of shear rate ($\dot{\gamma}$) and complex viscosity (η*) as a function of strain rate amplitude ($\gamma^0\omega$) at two strain amplitudes (γ^0 = 0.01 and 0.2) for coating colors containing standard delaminated kaolin at 66 wt.% solids



6. Static dewatering rates for the five coating colors

sions. Figure 4 reports results of strain sweep tests, normally used to define the linear viscoelastic domain. The complex modulus (G^*) is presented as a function of the strain. Note that the linear domain (approximately constant G^* values) is restricted to very small deformations ($\gamma^0 < 0.01$). This linear domain corresponds to solidlike viscoelastic behavior. The loss modulus (data not shown) is much smaller than the storage (elastic) modulus, which is almost equal to the complex modulus (viz., the phase angle is smaller than 10°). This elastic solid-type behavior is normally related to an elastic yield stress. Note that the complex modulus increases as the solids content decreases, which is again related to the higher quantity of CMC added to reach the same Brookfield viscosity.

In Fig. 5, the rheological data for steady-shear and oscillatory modes are compared in terms of the shear viscosity (η) and complex viscosity (η*) as functions of the shear rate ($\dot{\gamma}$) and strain-rate amplitude ($\gamma^0\omega$), respectively. The complex viscosity depends on the strain-rate amplitude and increases with the strain amplitude. At high strain, the plot of the complex viscosity vs. the strain-rate amplitude is analogous to that of the steady-shear viscosity vs. shear rate. The slope of approximately –1 (on a log–log plot) is indicative of a plastic flow behavior. This clearly shows that the elastic response is due to the particle–particle interactions, which in turn are responsible for the yield stress or the solid-type behavior of the suspension.

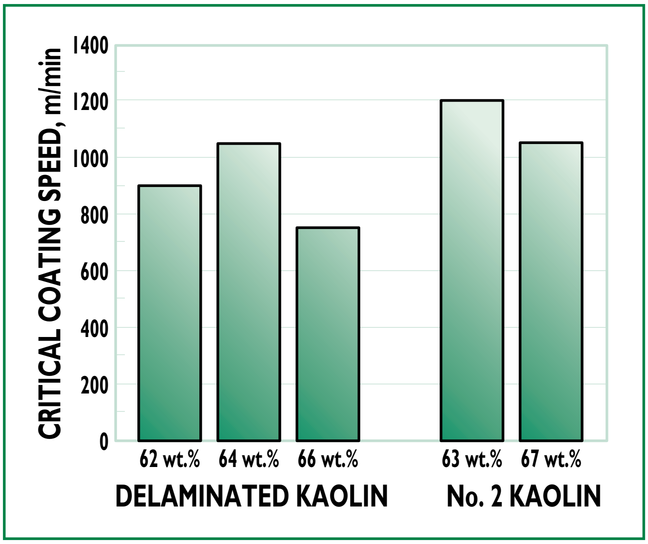
The results of Figs. 2 and 5 show that the low-shear viscosity data are essential for a strain-dependence analysis. Both figures give complementary information on interactions between components of the suspension. From our point of view, the low-strain rheological results are quite relevant for the industrial coating process. How do scientific rheological data obtained at low shear or shear rate relate to the real process? As mentioned before, the strain range covered in the coating process is small, and the time involved is very short. In a typical blade coater operating at high speeds, the coating color never reaches steady-state conditions from a rheological point of view. Hence, transient effects are highly relevant.

Measurements of static dewatering rates for the five coating colors are presented in **Fig. 6**. This test provides an interesting perspective of the interactions in the coating color. Comparing Figs. 3 and 6, it is clear that the highest critical stress was obtained for the formulation with the lowest static dewatering rate. In both cases, we have access to a global parameter that characterizes particle–particle and particle–CMC interactions *(2, 12)*. For a coating color with a higher "energy barrier," it becomes more difficult to remove water by static pressure. In other words, the dewatering rate measures the ability of the water to flow, which is strongly restricted if it is trapped within a structure.

Figure 7 reports the runnability results (critical coating speed) obtained on the CLC. The critical coating speed is the tangential speed of the coater when defects are first observed. The primary criterion used to define the critical coating speed was the appearance of coating bands or wet streaks *(22)*. Such defects are probably the most relevant with respect to rheology. Other defects such as bleeding were not observed. As shown in Table II, the Hercules end point for the vari-

KEYWORDS

Clay, coating color, coatings, kaolin, latex, measurement, minerals, rheological properties, runnability, shear stress, stresses, viscosity



7. Critical coating speed on the CLC for the five coating colors

ous coating colors is directly proportional to the solids content and does not correlate with the trend in the critical coating speeds on the CLC.

The coating results of Fig. 7 and the critical stress of Fig. 3 show a good correlation. The runnability increases linearly with the critical shear stress. This apparent correlation for five different formulations confirms our assertion that low-strain rheological properties are relevant in evaluating the behavior of coating colors.

CONCLUSIONS

Model studies suggest that coating runnability can be predicted by observing the low-strain shear rheology of the coating. The results presented here—based on five model coating colors containing standard No. 2 or delaminated kaolins—show that the critical stress observed at a very small strain correlated well with coating runnability. ("Critical stress" is defined as the maximum in the transient stress response in simple shear experiments.) Obviously, these results need to be confirmed for industrial coating colors, but similar experiments performed on typical coating colors tend to confirm the importance of small-strain stress growth behavior for the coating process.

The viscosity data obtained at steady shear rate for the five coating colors were very similar and thus could not be used to discriminate differences in runnability. However, small-amplitude oscillatory shear measurements revealed a linear viscoelastic domain, related to a rheological solidlike behavior. We have observed an analogy between the steady-shear-rate viscosity as a function of shear rate and the complex viscosity (at high strain) as a function of the strain-rate amplitude. This is typical of concentrated suspensions that depict a yield stress and plastic behavior. Measurement of transient shear showed a stress maximum that occurred at the same critical deformation for all the coating colors. The critical stress (maximum in the transient stress response in simple shear experiments) observed at a very small strain correlates well with coating runnability on a Cylindrical Laboratory Coater. Also, this stress peak correlates qualitatively well with the static dewatering rate. Obviously, these results need to be confirmed for industrial coating colors, but similar experiments performed on typical coating colors tend to confirm the importance of small-strain stress growth behavior for the coating process.

Small-strain experiments or transient viscosity measurements for small deformation provide a quick and convenient method for correlating coating runnability and formulation. Obviously, five coating color systems are not sufficient to provide a conclusive and quantitative relationship, but this new approach shows promise as a predictive technique for coating runnability. Further experiments are now being conducted using a high-deformation-rate "orifice rheometer." The suspension through this orifice undergoes a very high deformation rate, but the strain remains very small. Preliminary results using this rheometer will be presented later. **TJ**

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The authors are grateful for the efforts of Steve Brown and Steve Kittleson at Engelhard Corp. Thanks also to management at Engelhard Corp. for funding the study.

Received for review March 9, 1996.

Accepted March 7, 1997.

Presented at the TAPPI 1996 Coating Conference.

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