Research Article

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Correlating Coating Quality of Coverage with Rheology for Mica-Based Paints

<https://doi.org/10.1515/arh-2020-0110>

Received May 29, 2020; accepted Dec 02, 2020

Abstract: This paper examines the relationship between rheology and the qualitative appearance of dried, mica-based paint coatings used in the aerospace industry. The goal is to identify key rheological characteristics indicative of poor coating visual appearance, providing a screening tool to identify unsatisfactory paint formulations. Four mica paints were studied, having coating visual appearances ranging from very poor to very good. Strain sweeps indicated that the poor-quality paints have a smaller % strain midpoint in the linear visco-elastic range; while the good-quality paints have a lower G'/G'' cross-over point in frequency sweeps. Thixotropy experiments utilizing single and multiple-loop hysteresis cycles plotting shear stress as a function of shear rate showed that the base mica paints with good appearance had nearly constant, reversible profiles in the forward and the backward directions; while the mica paints with poor appearance were irreversible with a noticeable gradual change in shear stress as more loops are run. The difference in area between the forward and the reverse curves was determined, leading to a quantifiable criterion that can differentiate good paints from poor paints with significance testing. This work would establish the first rheology model using hysteresis loops to predict the visual properties of mica-based paints.

Keywords: mica-based paint, thixotropy, hysteresis experiments, paint quality

1 Introduction

Angle-dependent, optical coating effects can be found in many industrial products and film applications [1]. Among the many end-user applications, these effects are used for decorative purposes within coating systems employed in the automotive and aerospace industries. Angle-dependent, optical effects in coating films can be achieved through the use of special-effect pigments [2–4]. There are significant advantages from the use of special-effect pigments in decorative applications such as the illusion of optical depth, the ability to imitate the effect of natural appearance, or even to change color depending on the viewing angle [5]. Some of the main types of special-effect pigments include metal-effect pigments [6], optical interference-effect pigments [7], fluorescent pigments [8], and luminous pigments [9].

Although substrate-free pigments (e.g. metal-effect pigments) [10, 11] are commercially available, they can be brittle, mechanically unstable, and be limited by their chemical composition. Therefore, substrate-based-effect pigments that are more robust have also been developed for use on industrial products within more demanding working environments. Special-effect, mica paint systems are one such example used in the automotive and aerospace industries with the additional benefit to reflect/shine light from the surface so as to create a distinctive, attractive visual effect. Mica increases flop – characteristic impression of light reflected between the angle of incidence and the angle of observation.

These paint systems (consisting of primer, basecoat, and finish topcoat) contain mica flake particles typically found in the base layer or sometimes even in protective clearcoats to increase the reflectance of the paint once it has dried. The mica particles are dispersed within a liquid paint suspension due to a combination of colloidal, hydrodynamic, and polymer-mediated forces. The composition of the paint vehicle (solvent and other additives) controls these forces. Shear and gravity forces cause the particles to move relative to each other. Depending on the balance of inter-particle forces, the particle distribution can become heterogeneous, especially if aggregation occurs. The irre-

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versible change in localized particle concentration due to mica particle migration is a major cause of mottling, which is a color variation problem due to uneven distribution of particles across a surface of known length scale. Mottling can be induced by a combination of shear forces during both application and drying processes. When a finished part exhibits visual defects, it decreases the value of the product, and must be re-painted. This adds costs and delays product completion dates.

Herein, we investigate the relationship between rheology and visual appearance for polyurethane-based, mica paints used in the aerospace industry. The work primarily studies paint structure in relation to appearance behavior, assuming influence from process and application factors are constant for simplicity because they are mostly the same regardless of paint type. As a result, we focused on a low shear range typically found during drying, recognizing the fact that trends found at low shears can be extended to high shears such as painting as discussed later on in the paper. Mottling due to the formulation of the paint itself, the biggest unknown variable, could be caused by non-uniform particle size, density mismatch between the mica particles and the solvent, and changing particle orientation during the drying process [12, 13]. Despite the importance of particle (flake) orientation in the color properties of paints and the numerous experimental and theoretical works published in the literature [14–17], the mechanism of flake orientation is still not very well understood.

Several characterization methods have been used to study paint. Techniques including mechanical profilometry and optical measurements [18], along with microscopy and spectroscopy, have been utilized [19, 20]. Among the various microscopy techniques, scanning electron microscopy (SEM) has been utilized with great success [21]. A specular gloss, distinctness of image, and orange peel correlation with BYK instrumentation has been established for automotive paint appearance [22, 23]. Rheology has also been employed to study non-colloidal suspensions and to establish particle concentration profiles [24]. The rheological influence of mica incorporation in blends including identifying any trends in log-log plots of shear stress vs. shear rate and viscosity vs. shear rate has also been examined [25].

In earlier work using shear stress measurements, we suggested that non-colloidal spheres in suspension acquire an anisotropic arrangement that depends on the direction of shear, and that a transition between the two arrangements is seen when the direction of shear is reversed [26]. Here, we planned on utilizing shear-reversal experiments to model shear-induced, time-dependent structure formation of the mica particles within the paint suspensions. After experimentation, we discovered that the flaked particles

were poly-disperse, non-colloidal, irregular-shaped particles and that the shear-reversal experiments would not be suitable for developing a predictive appearance model.

The potential for using thixotropy experiments to model paint behavior has been previously discussed [27–29]. In one example, a hysteresis loop of viscosity versus shear rate was used to model thixotropic behavior [27]. The concepts of multi-step, hysteresis loop experiments with area extrapolation [27] were used in combination with a shear stress over time study [26] to create a new hysteresis experiment that modeled shear stress versus shear rate. Additionally, rheology has been utilized to characterize special-effect paints containing mica [30]. A cone-and-plate geometry and multiple test protocols were used to characterize rheological variables in water-based paints [30], with the work serving as a guide on how to plot the hysteresis graphs and to determine basic procedures for the shear experiments.

As new mica-based paints are developed, having a screening tool to predict paint appearance with a quick, simple test that requires only a small volume of sample would be very beneficial. This study focuses on using rheology to correlate observable rheological characteristics with the quality of paint appearance. Thixotropic experiments utilizing a hysteresis loop of shear stress as a function of shear rate provide a unique insight into the structure and the behavior of mica paint systems with known quality. This work establishes the first rheology model using thixotropy experiments with hysteresis loops to predict the visual properties of mica-based paints.

2 Experimental Procedures

2.1 Equipment

A TA Instruments AR 2000 parallel plate rheometer, with a temperature controlled peltier plate, and a 50 mm steel plate geometry, was used for this study. The paints were mixed using a Rockwood pneumatic paint shaker.

2.2 Materials

Four different special-effect, solvent-based mica paints as listed in Table 1 were studied to determine any differences in rheological properties, with photographs of each paint's appearance tendency also shown in Figure 1.

Table 1: List of mica-based paint systems used.

Product Name	Suspension Base	Mica Particle Size (μm)	% Solids	Dry Mica Paint Consistency in Quality of Coverage (by Visual Appearance*)
Mica Gold	Solvent	10-60	72-76%	Very poor
Mica Silver	Solvent	5-100	68-73%	Somewhat poor
Mica White	Solvent	50-60	65-70%	Good
Mica Clear (mica control-no color)	Solvent	100	62-67%	Very good

*Overall visual assessment as determined by a Boeing team consisting of production and color laboratory.

Figure 1: Near surface photographs of mica-based paint systems with particle size reference listed in Table 1 – Mica Gold (upper left), Mica Silver (upper right), Mica White (lower left), and Mica Clear (lower right).

2.3 Methods

For all rheology experiments listed below, a gap of 1,000 microns was used to minimize the effect of particle size on the data collection.

Strain sweep:

Strain sweeps ranging from 0.01-100% were ran at 25°C with a frequency of 1 Hz to determine the linear visco-elastic region (LVER) of the paints. The frequency sweeps and the thixotropic experiments were performed at percent strains that are near the center of the LVER for each respective paint.

Frequency sweep:

Frequency sweep tests were carried out to study the point at which the storage and the loss modulus intersect (the visco-elastic cross-over point). These sweep tests were conducted from 1-60 rad/s, 25 points per decade (ppd), and at 25°C. This test showed the angular frequency at which the elastic forces dominate over the viscous properties or vice versa.

Thixotropy:

Thixotropic studies were performed utilizing a single hysteresis loop of shear stress versus shear rate. The shear rate was varied in between 0-1 1/s. This shear rate region was chosen to simulate the shear effects that occur on a paint during the drying process [31]. These experiments had two steps: one, shear rate increasing from 0-1 1/s (*i.e.* forward), and two, shear rate decreasing from 1-0 1/s (*i.e.* backward or reverse). These tests were conducted on the complete paint mixture (base, activator, and thinner components all mixed together); and also on the base component (without activator and thinner) containing the mica particles and colored pigments. The other experimental parameters were 10 ppd, 25°C, 10 seconds sample period, 5% tolerance within three consecutive measurements, and a maximum point time of one minute.

Additional thixotropic experiments were performed with a double hysteresis loop and a quadruple ('quad') hysteresis loop. These runs consisted of a single hysteresis loop with shear rates varying from 0-1 1/s and then from 1-0 1/s, and then repeated a second time for the double hysteresis loop, and three more times for the quad hysteresis loop. There was a two-minute equilibrium pause time between the loops. These experiments were conducted at 10 ppd, 25°C, 10 seconds sample period, 5% tolerance within three consecutive measurements, and a maximum point time of one minute.

3 Results and Discussion

The strain sweep runs as displayed in Figure 2 illustrate the LVER range for each paint system (base, activator, and thinner components added and mixed together) based on the G'/G'' curves, which were flat approximately between 0.05% and 10%. The reported LVER percent strain was in the middle of the linear, flat region: Mica Gold at 0.1% strain, Mica Silver at 0.5%, Mica White at 1%, and Mica Clear at 5%. Moduli outside of the LVER range indicates non-linearity, or that the applied % strain is either too low or too high to accurately measure material structure. Notice, qualitatively speaking, a trend following Table 1 – the lower quality paints (rejectable level of visual defects) have a lower LVER (well below 1%), while the better paints (acceptable level of visual defects) tend to have higher values. The % strain was held constant during the frequency sweeps (and the hysteresis experiments later on) at the optimal value taken from the LVER in Figure 2. The frequency sweeps in Figure 3 illustrate that both Mica Gold and Mica Silver, the poor quality paints, initially exhibited a higher G' than G'' (elastic forces dominating) with a high G'/G'' cross-over point well beyond 10 rad/s. Conversely, the better paints, Mica Clear and Mica White, had a cross-over point shift to lower frequencies (closer to 1 rad/s), with the viscous forces dom-

inating thereafter. This trend is of value in identifying good versus poor-quality paints by use of a frequency sweep. As compared to the LVER findings, the extremes have now somewhat flipped: poor paints have a high moduli cross-over, while good paints have a low cross-over point. Paints that can dissipate more readily than storing energy will have better physical properties because it has more relaxation ability.

The thixotropy experiments initially examined the base, activator, and thinner paint mixtures. A hysteresis loop was utilized at low shear rates ranging from zero to one and then one back down to zero 1/s at 25°C in the designated strain LVER. As illustrated in Figure 4, the suspensions were stable because the shear stress profiles became mostly reversible. It is noted that Mica Gold, and to a lesser extent Mica Silver, do show some deviations at higher shear rates, but the difference isn't sizable enough to quantify or to pursue for further study.

Interestingly, when evaluating just the paint base, as shown in Figure 5, a much more clear insight in connecting rheology to the quality of the paint appearance was found. This single-loop hysteresis test showed that the poor paints, Mica Gold and Mica Silver, have different shear stress curves that didn't coincide directly onto each other in the forward and the backward directions like the good paints Mica Clear and Mica White. This apparent permanent change in struc-

Figure 2: Strain sweeps ranging from 0.01 to 100% to determine the LVER (using the 'flat' or linear portion of the moduli curves), as shown in green text for each individual paint at 25°C.

Figure 3: Frequency sweep from 1-60 rad/s at 25°C (% strain LVER shown in parenthesis).

Figure 4: Single-loop hysteresis experiments at 25°C for each mica base paint with their respective activator and thinner components added and mixed together. A shear rate from zero to one 1/s in the forward direction is shown, and a shear rate from one to zero 1/s in the backward direction is also shown.

Figure 5: Single-loop hysteresis experiments at 25°C for each mica base paint without their respective activator and thinner components added and mixed together. A shear rate from zero to one 1/s in the forward direction is shown, and a shear rate from one to zero 1/s in the backward direction is also shown.

Figure 6: Double-loop hysteresis experiments at 25°C for each mica base paint without their respective activator and thinner components added and mixed together. A shear rate from zero to one 1/s in the forward directions are shown, and a shear rate from one to zero 1/s in the backward directions are also shown. There was a two-minute equilibrium pause time between the loops.

ture is indicative of either localized aggregation of mica particles or non-uniform particle size/orientation, key contributors in observing mottling on painted surfaces. The base components of Mica Gold and Mica Silver underwent irreversible changes in shear stress with variable shear rate.

The Mica Clear paint was completely reversible by following the identical shear stress pathway in both the forward and the backward directions. Mica White mostly resembled this trend, but was observed to have a preshear conditioning step before plateauing to a reversible equilibrium state starting at a shear rate of ~ 0.001 1/s in the forward direction. The reversibility/irreversibility of this shear stress profile in Figure 5 correlates well with the paints suspension uniformity and the quality of appearance after it has been sprayed. This is a logical derivation because structure is a function of particle orientation and collision effects. Since Mica Clear and most of Mica White were reversible, they exhibit a high level of structure recovery. Mica Gold and Mica Silver followed the opposite trend. Consequently, the reversibility in the thixotropic loop of the base paint component appears to be a key indicator for predicting the visual quality of the final paint coating. This result is in good agreement with previous works. A thixotropic, time-dependent rheology model was developed for commercial marine paints identifying different hysteresis areas between up-down curves, each requiring for unique application [27]. Similarly, percent viscosity recovery as measured by hysteresis is an important parameter in determining flow-levelling and sag resistance for waterborne, latex paints used in architectural coatings [32]. Our study targeted the low end of the defined shear rate spectrum for paint flow and sag that becomes more increasingly magnified as approach higher shears above 1 1/s [31]. The levelling of thixotropic coatings driven by surface tension has been modeled in a stepwise, linear calculation fitted using five parameters for both steady-state and transient rheology [33].

To further validate the single-loop results, double-loop hysteresis experiments were performed on the mica base and are displayed in Figure 6. The same trends were observed as in the single-loop results from Figure 5. The shear rates in the forward and the backward directions were also from zero to one 1/s and then from one to zero 1/s respectively in the double-loop hysteresis runs. The shear stress lines in the forward and the reverse directions for Mica Gold and Mica Silver also didn't overlap over each other in the second hysteresis loop, exactly like what was seen in the first loop in both Figures 4 and 5. As a matter of fact, the stress levels increased in Mica Gold, the worst quality mica paint, when comparing forward to forward and backward to backward plots. Mica Silver, the second worse

quality mica paint, seemed to exhibit the opposite behavior in the second loop as the shear stress in the forward direction decreased, but held steady in the backward direction. Meanwhile, Mica White, rated as the second best quality mica paint (behind the Mica Clear control), now has the pathways much closer together with little difference between the two loops aside from the initial forward run which basically acts as a preshear conditioning step prior to reaching a leveled, equilibrium state. Finally, Mica Clear, the best mica paint, had no distinction whatsoever in all directions in both hysteresis loops (consistent with the single-loop plot in Figure 5). These results reveal a pattern: paints characterized as having a good appearance show thixotropic profiles with a negligible difference in area between the forward and the reverse directions. Conversely, paints with poor appearance have noticeable differences in area that increase for paints that have more quality issues.

Furthermore, quad-loop hysteresis runs conducted on the base mica at 25°C as shown in Figure 7 support the single and the double-loop results. Additional hysteresis cycles magnify the comparison between the quality of the paints: irreversible profiles that have a gradual increase in shear stress on the y-axis between each successive forward/backward directions characterize paints of low-quality appearance (such as Mica Gold and Mica Silver); while nearly constant, reversible curves at smaller shear stresses are a property of high-quality paints (such as Mica Clear and Mica White). This is indicative of the entropy disorder that is created in the structure of the base components containing the mica particles in the poor-quality paints. It is speculated that even more hysteresis cycles (not studied in this work) would continue this trend.

To develop a more quantitative predictive rheology model, t-test significant differences in area were taken with respect to the control paint, Mica Clear, and confidence levels were established from a statistical table. The areas under the forward and the backward hysteresis curves were computed by simply taking the Δx (shear rate) multiplied by the average y (shear stress) between successive data points and then taking the overall sum underneath each curve. The absolute area difference between these two curves was determined for each mica base paint and then compared to the difference from Mica Clear using Welch, independent two-sample t-testing. Table 2 includes the average areas and the t-test results of three distinct datasets: top - the first forward/backward loop in the single (Figure 5), double (Figure 6), and quad (Figure 7) hysteresis runs; middle - shortened, single-loop hysteresis experiments (to reduce time; with triplicates) of the mica base component with a shear rate ranging from $0.001 - 1$ 1/s and then in reverse from $1 - 0.001$ 1/s (all other experimental

Figure 7: Quadruple-loop hysteresis experiments at 25°C for each mica base paint without their respective activator and thinner components added and mixed together. A shear rate from zero to one 1/s in the forward directions are shown, and a shear rate from one to zero 1/s in the backward directions are also shown. There was a two-minute equilibrium pause time between the loops.

parameters remained the same); bottom - all four loops in the quad (Figure 7) hysteresis runs.

In analyzing Table 2, it can be seen that the two mica paints with poor visual properties, Mica Gold and Mica Silver, have average areas greater than 0.10 between their respective forward and backward shear stress curves with significance confidence levels of at least 90% regardless of the type of hysteresis experiment performed. Further inspection reveals that long time scales (*i.e.* the quad hysteresis runs) seem to produce the same quantitative t-test statistical result as short time scales (*i.e.* the shortened single hysteresis runs) with minimal fluctuation, and that long time scales appear to have the areas and confidence levels more qualitatively fit in sequence with the ranking of the paints by visual properties back in Table 1. The drying process in reality is much longer, and with time, the paints seem to follow a clear trend in distinguishing poor from good quality paints.

Meanwhile, the two mica paints with good appearance, Mica White and Mica Clear (the control), had average areas below 0.05 in Table 2. In two of the three datasets, Mica White actually had a lower area than Mica Clear, denoted with a *, leading one to conclude that the difference is significant. In reality, because the Mica White area is smaller than the control, it really means that the Mica White is a

good paint rather than implying it is a ‘statistically significant’ poor paint. It can be interpreted to be a good paint, just on the opposite end of the comparison spectrum. In the other dataset, Mica White had a 50-75% significant difference on the low-quality paint side (*i.e.* 25-50% high-quality). In some ways, the trend identified for poor paints holds true with good paints in that using more hysteresis cycles seem to further validate the paint quality in-line with the observed visual characteristics. Therefore, it can be asserted that both Mica White and Mica Clear should be good paints, matching with Table 1.

Upon a closer review of the single-loop hysteresis plotted in Figure 5, it looks like that Mica Gold should have a larger area between the curves than Mica Silver. However, the non-quad hysteresis datasets in Table 2 say the opposite. This is because the shear rate values on the x-axis are skewed because it is based on a power of ten, and not drawn to scale. The irreversibility as seen in Figure 5 becomes more pronounced at lower shear rates near zero, meaning that those summed areas in reality are negligible. So, although very useful in identifying mottled paints by visual observation, in the area/t-test calculations, it doesn’t make a significant contribution. Greater separation between the forward and the backward curves occurs closer to one 1/s shear, and would be even further pronounced at much higher shear

Table 2: Average area calculation between the forward and the backward hysteresis curves for each mica base paint with corresponding t-test significance confidence level in comparison to Mica Clear control paint at 25°C.

Loop 1 in single, double, and quad hysteresis runs				
Base Component	Average Area	Standard Deviation	Number of Data Points	t-test Significance Confidence Level
Mica Gold	0.1844	0.1459	3	at least 90%
Mica Silver	0.3693	0.0856	3	at least 99%
Mica White	0.0321	0.0280	3	between 50–75%
Mica Clear (control)	0.0240	0.0107	3	–

Single hysteresis triplicate runs (shortened time scale)				
Base Component	Average Area	Standard Deviation	Number of Data Points	t-test Significance Confidence Level
Mica Gold	0.2008	0.0550	3	at least 97.5%
Mica Silver	0.3597	0.0155	3	at least 99.9%
Mica White	0.0159	0.0144	3	at least 90%*
Mica Clear (control)	0.0358	0.0170	3	–

All loops in quad hysteresis runs				
Base Component	Average Area	Standard Deviation	Number of Data Points	t-test Significance Confidence Level
Mica Gold	0.3817	0.2480	4	at least 96%
Mica Silver	0.1410	0.0919	4	at least 93.5%
Mica White	0.0133	0.0098	4	at least 99.5%*
Mica Clear (control)	0.0412	0.0039	4	–

*indicates a negative area difference of Mica White in comparison to Mica Clear

rates typically found in painting application processes [31]. We hypothesize that the area ratios between the paints would be relatively proportional in scale as a function of shear resulting in equivalent statistical test significance, meaning that rheology trends observed at lower drying shears would also apply at higher application shears as well. In addition, the more cycles added in the hysteresis experiments, the more accurate the reflection exists generally speaking between the area/t-test values and the quality of paint appearance. One loop is also sufficient to make a suitable determination for ease and simplicity as a screen test. Additionally, for the quad hysteresis experiments in Figure 7, the difference in area between each successive forward line and between each successive backward line appear to actually be greater than the difference between the forward and the backward curves within the particular individual loops. These numbers were not computed.

The numerical criterion in this work can be quite a valuable tool, especially in researching new paint formulations or when different processing conditions are selected in a painting application. When the integrated area encased by the hysteresis loop curves exceeds 0.10 with a positive sign relative to a control paint (of good quality) and has at least a

90% significance difference, our developed model suggests that the paint will most likely have poor visual properties. As a result, either another paint system should be used, or that the formulation itself should be adjusted until the area is reduced below 0.05 that subsequently changes the net area difference to a negative value when subtracting from the control baseline, with each additional hysteresis loop repeatedly showing reversibility forwards and backwards.

4 Conclusions

Mica-based paints were characterized by rheology to connect quality of appearance to recognizable trends. This work establishes a practical predictive model, consisting of the following findings:

1. Strain sweeps indicate that the poor-quality paints have a smaller % strain midpoint in the linear visco-elastic range.
2. Frequency sweeps reveal that the good-quality paints have a lower G'/G'' cross-over point.

3. Single and multiple-loop hysteresis experiments performed at 25°C showed that the base mica paints with good appearance had nearly constant, reversible profiles in the forward and the backward directions; while the mica paints with poor appearance were irreversible with a noticeable gradual change in shear stress as more loops are run. This establishes a visual qualitative check for quick and easy determination. Longer time scales (*i.e.* more loops) appear more accurate with appearance properties as it mimics the actual drying process. Addition of activator and thinner components have a slight marginal effect, but not distinguishable enough to differentiate between the paints.
4. Extrapolation underneath the hysteresis curves quantified the difference in area between the forward and the reverse lines. In three unique datasets, the low-quality mica paints had an area exceeding 0.10, in contrast to the high-quality mica paints which were below 0.05. Using significance testing, a statistical criterion can effectively distinguish poor-quality paints when the net area difference is *positive* in reference to a control baseline with at least a 90% confidence level regardless of how many loops are run. The same methodology also applies for a negative area difference, implying that the paint is high-quality.
5. Rheology aside, although particle size appears to be a non-factor from Table 1, we note that % solids scales very well inversely with quality of paint finish observed.

Acknowledgement: This work was funded by Boeing Research & Technology in a collaboration effort with the University of South Carolina. The authors acknowledge Ryan R Anderson, Doug Berry, Glenn Dalby, Mike Rice, Jill Seibergh, and Dara Ung for providing technical guidance and support in this work.

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