

Rheological Characteristics of Platy Kaolin

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ABSTRACT

Platy kaolin can provide significant value in the coating of paper and paperboard. It can be used in multiple applications, and provide benefits such as TiO₂ extension, smoothness improvement, improved print gloss or ink set rates, calendering intensity reduction, and improved barrier properties. It is not a pigment that can be simply substituted for traditional hydrous kaolin without some adjustment to the coating formulation. These adjustments can be as simple as reducing solids but may require binder changes as well. The coater set up may need to be adjusted because of the unique rheological behaviors these pigments exhibit.

The rheological characteristics of platy kaolin are explored here. This includes high shear and low shear viscosity, oscillatory measure of viscoelasticity and water retention measurements. An extensive analysis reveals some unique behaviors that need to be understood when utilizing these materials. The degree of shear thinning behaviors is investigated using the Ostwald de-Waele power law. The immobilization point was determined using the Dougherty-Krieger (1-4) equation and related to Weeks' (5) work on blade coater runnability. An indirect measure of particle shape and size synergy is also demonstrated using the Dougherty-Krieger equation parameters.

INTRODUCTION

Platy kaolin has unique rheological characteristics that require consideration when formulating with them. Their high shape factor or ratio of the diameter of a particle to its thickness means it has a larger sphere of rotation than a measurement of its particle size would indicate by use of a Sedigraph measurement. This means it takes up more space in a turbulent flow field than would be expected, but a lesser profile in laminar flow. It also means that these platy particles will interact physically with blockier pigments like ground calcium carbonate, calcined clay and precipitated calcium carbonate more than their blockier counterparts. This interaction not only results in unique rheological characteristics, but also in unique packing structures that impart enhanced optical scatter, higher coating bulk and improved surface coverage. Even without being married to a blockier counterpart the higher particle plate diameter gives unique coverage, smoothening and even barrier properties.

It is well known that a blade coater's operating window depends upon the viscous properties of the coating. There are a number of issues that can be related to the rheological characteristics of the coating such as weeping, whiskering, coat weight control, scratches and streaks. Stable operation of a blade coater also requires good control of the rate of dewatering of the coating. Rod coaters may have similar issues as blade coaters that are usually manifested as spits and accumulated deposits on the rod. Metered Size Press coaters have a complex set of needs to run properly related to the rheological characteristics of the coating such as misting, orange peel and rod/blade metering defects or film thickness control. Curtain coaters have an operating window that depends upon the viscosity of the coating under low shear, the extensional viscosity and surface tension of the coating.

The TAPPI Roll and Web Defect Troubleshooting Guide (6) lists the common causes of whiskering on a blade coater. Figure 1 shows a photographic example at the outgoing side of the blade coater blade tip. They are: 1) coating solids too high, 2) poor water holding properties of the coating, 3) high coating line speed, 4) improper blade and/or blade geometry (blade angle too low), 5) blade bevel not running parallel to the web, 6) overly absorbent

web, 7) blade pressure too high, 8) new blade not worn in yet, 9) excessive dewatering between application and metering points, and 10) too high a chamber pressure on a short dwell coater. All of these can be related to the fundamental properties of the coating and base paper. Here we will focus on the rheological characteristics of the coating.

Weeks (5) recently has presented a study of the coating characteristics that affect blade coater runnability based upon her PhD dissertation work at the U. Maine. One of the outcomes of the work was to add clarity to the understanding of what coating solids can be run on a blade coater at a given speed while avoiding such issues as streaks, weeping, whiskering and scratching. It was clearly identified that the maximum web speed is linearly related to the difference of the immobilization solids and the coating solids. The plot shown in Figure 2 is from her work. This set of data was generated on a CLC-2000 laboratory coater.

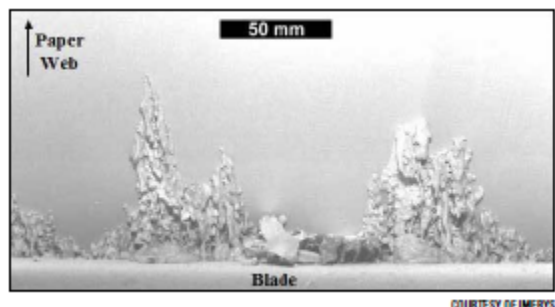


Figure 1: Whiskering at the outgoing side of the blade tip as shown in the TAPPI Ultimate Roll and Web Defect Troubleshooting Guide (6).

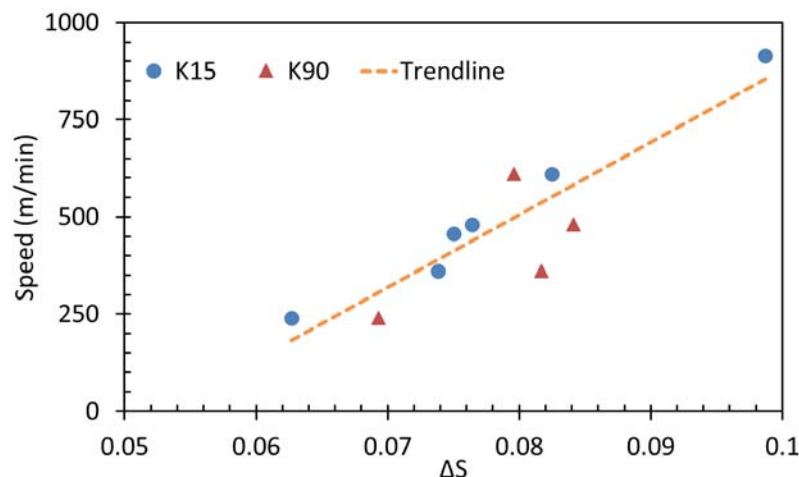


Figure 2: Plot of the maximum speed without coating defects that can be run, as function of ΔS . ΔS is the immobilization solids minus the coating solids. K15 is a 15 shape factor kaolin pigment and K90 is a 90 shape factor kaolin pigment.

The viscosity of a coating depends upon the shear rate at which it is measured and the geometry of the measuring device. A bob and cup, capillary, cone plate and plate, or spindle in a cup are each imparting a different flow field to the coating as well as having different levels of shear that can be applied. These geometries will all be evaluated in this piece of work.

The change in solids of a coating while being run on a coater is often cited as a cause of operating issues. One obtains a different picture depending on whether a static or dynamic measure is made. In a static measure the plates will act as a resistor the flow of water out of the coating. This may or may not apply to what is happening around a dynamic coating process. The dynamic measure gives us richer information in that it indicates the rate of rise of viscosity as the coating dewaters.

Viscoelasticity is often cited as being a cause of coating runnability issues. A common method to assess it is the use of a cone and plate geometry which is oscillated at a range of frequencies. The phase shift of the force response of the oscillation input is a way of characterizing whether a fluid or material is elastic, viscous or a combination of the two.

In this study the Dougherty-Krieger equation (7) or method was used to determine the maximum solids of the coating. These calculated maximum solids can be considered to be the immobilization points of the coatings. This can then be used to determine the Weeks ΔS parameter for the coatings studied. The smaller that ΔS is, as already explained by the Weeks work, the smaller the operating window is on a blade coater. It can also be speculated that this parameter can be indicative of whether there will be a runnability issue with the rod applicator on a metered size press.

The Dougherty-Krieger equation is based upon the Einstein equation that accounts for particle crowding effects in a suspension. The viscosity of a suspension as a function of solids using the Dougherty-Krieger equation is $\mu = \mu_0 / (1 - \frac{\phi}{\phi_{max}})^{\alpha \phi_{max}}$ where μ is the apparent viscosity, μ_0 is the viscosity of the suspending medium, μ is the measured viscosity, ϕ is the volumetric solids of the coating, ϕ_{max} is the maximum solids and α is referred to as the Einstein coefficient or the intrinsic viscosity. Using apparent viscosity versus volumetric solids data μ_0 , ϕ_{max} , and α can be solved for in the non-linear equation using the solve Add-in in Excel. In order to do that a minimum of 3 sets of solids and apparent viscosity pairs are required.

Most coatings used in the production of coated papers are power law fluids of various degrees of shear thinning behavior. The constitutive viscosity power law relationship to the shear rate can be expressed as $\mu = \mu_{FC} \dot{\gamma}^{(n-1)}$ where μ is the apparent viscosity, μ_{FC} is the flow consistency index and n is the flow behavior index. This power law relationship is also referred to as the Ostwald-de Waele power law. This law will be applied to the cone and plate and capillary viscosity data collected here.

The Dougherty-Krieger and Ostwald-de Waele relationships were investigated not only as a way to model the data and determine the immobilization point of the coating. Each was investigated as a way to indicate whether there is an optimum synergistic structuring of coating because of the blending of blocky (GCC) and various platy (kaolin) pigments.

MATERIALS

Table I summarizes a set of kaolin pigments that were selected for this work that has a broad range of particle sizes and shape factors. The size of the pigments was determined using a Sedigraph and brightness was determined using the TAPPI standard T646. Shape factor is a measure of the ratio of the average diameter divided by the average thickness of the particles as measured by a stop flow conductivity instrument developed by Imerys (8). The physical characteristics of these pigments are listed in Table I. FGCC is a fine ground calcium carbonate, FK is a fine regular brightness kaolin, DELK is a typical delaminated kaolin, FPK is a fine platy kaolin, MPK is medium platy kaolin, CPK is a coarse platy kaolin, and UPK is an ultra-platy kaolin. The pigments used in this work can be obtained from

Imerys. An SBR latex (620NA) from Trinseo was used that has a Tg of $\sim 10^0$ C and a median particle size of 0.18 microns and identified as SBR in this paper. A high and a low molecular weight ethylated starch was used in this study. They are PG 260 (high molecular weight) and PG290 (low molecular weight) and are identified as HMS and LMS. They are supplied by Penford (a subsidiary of Ingredion). Sodium hydroxide was used to adjust the pH of the coatings.

Table-I: The important physical characteristics of the pigments utilized in this work. Please note that the shape factor of the FGCC is attributed as an approximation for analysis purposes rather than measured.

	FGCC	FK	DELK	FPK	MPK	CPK	UPK
%Solids	74.9	70.8	67.4	62.9	62.1	58.2	56
TAPPI Brightness	96	88	88	89	87	88	87
Shape Factor	2	14	35	58	77	83	97
pH	8.4	6.8	6.7	6.4	7.0	7.6	7.0
% < 2 micron	92	93	83	91	73	61	65
% < 0.25 micron	2	49	34	29	21	16	14
d50 in microns	0.66	0.26	0.39	0.43	0.84	1.63	2.50

FORMULATIONS, EXPERIMENTAL PLAN AND METHODS

The coatings were made down in a high shear mixer from pigment slurries. The starches were cooked in a laboratory batch cooker. The latex binder was used as received. Table-IIa, b, c and d show the formulations that were studied. Each grouping has a different purpose. The first group is a comparison of each of the pigments studied as 100% of the pigment in the formulation; the second group is a comparison of the kaolin pigments combined with the FGCC at a 50:50 ratio; the third group looks at the CPK pigment at a 50:50 ratio with the FGCC with variations in binder ratios and starch molecular weight; and the fourth looks at the FPK pigment at a 50:50 ratio with the FGCC with variations in binder ratios and the starch molecular weight. The purpose of these groupings is to understand how the pigment shape factor of the various kaolin pigments interact with a blocky co-pigment to affect the rheology. The effect that changes in binder with the 50:50 combinations have on the rheological characteristics of the FPK and CPK containing coatings were also investigated. All of the coatings were made down at the highest solids possible and then diluted twice. Each dilution was at about a 2% change.

Table IIa: Coating formulations for the comparisons of 100% of each of the pigments. The solids ladder of each formulation is also indicated.

	100FGCC	100FK	100DELK	100FPK	100MPK	100CPK	100UPK
FGCC	100						
FK		100					
DELK			100				
FPK				100			
MPK					100		
CPK						100	
UPK							100
Latex (L)	8	8	8	8	8	8	8
LMS	8	8	8	8	8	8	8
HMS	0	0	0	0	0	0	0
pH	8.1	8.1	8.1	8.1	8.1	8.1	8.0
Solids1	66.1	62.7	60.6	57.6	56.9	54.5	52.7
Solids2	64.2	60.8	58.8	55.6	55.1	52.3	50.5
Solids3	62	59	56.7	53.8	53.1	50.5	48.6

Table IIb: Coating formulations for the comparisons of the 50:50 blend combinations. The solids ladder of each formulation is also indicated.

	50:50FK	50:50DELK	50:50FPK	50:50MPK	50:50CPK	50:50UPK
FGCC	50	50	50	50	50	50
FK	50					
DELK		50				
FPK			50			
MPK				50		
CPK					50	
UPK						50
Latex (L)	8	8	8	8	8	8
LMS	8	8	8	8	8	8
HMS	0	0	0	0	0	0
pH	8	8	8	8	8	8
Solids1	64.7	63.6	61.6	61.4	60.1	58.4
Solids2	62.8	61.5	59.7	59.2	58.1	56.3
Solids3	60.7	59.3	57.6	57	56	54.4

Table IIc: Coating formulations for the 50:50 FGCC and CPK binder variations. The solids ladder of each formulation is also indicated.

	CPK+8LMS	CPK+8HMS	CPK+10L+4HMS	CPK+10L+4LMS	CPK+12L
FGCC	50	50	50	50	50
FK					
DELK					
FPK					
MPK					
CPK	50	50	50	50	50
UPK					
Latex (L)	8	8	10	10	12
LMS	8			4	
HMS		8	4		
pH	8	8	8	8	8
Solids1	60.1	60.4	62.1	61.9	64.3
Solids2	58.1	57.9	60.1	59.8	62.3
Solids3	56	55.9	58.2	57.8	60.3

Table IId: Coating formulations for the 50:50 FGCC and FK binder variations. The solids ladder of each formulation is also indicated.

	FK+8LMS	FK+8HMS	FK+10L+4HMS	FK+10L+4LMS	FK+12L
FGCC	50	50	50	50	50
FK	50	50	50	50	50
DELK					
FPK					
MPK					
CPK					
UPK					
Latex (L)	8	8	10	10	12
LMS	8			4	
HMS		8	4		
pH	8	8	8	8	8
Solids1	64.7	65.7	68	66.9	70.0
Solids2	62.8	63.6	65.6	64.8	68.0
Solids3	60.7	61.5	63.7	62.6	66.1

Various viscosity measurements were made. Low shear rate measurements were made using a RVT Brookfield at 20 and 100 rpm with a #5 spindle. It is understood that not utilizing a lower numbered spindle for the 20 rpm measurements is problematic. This was an oversight in retrospect, but the main outcome of that was in limiting our ability to measure the higher viscosity coatings at 20 rpm. High shear measurements were made using a DV-10 Hercules at 4400 rpm using the E bob. An Anton-Paar with a cone and plate configuration was used at a range of shear rates up to 1000 s^{-1} . The Anton-Paar with a cone and plate configuration in oscillatory mode was also used to determine the viscoelastic properties. An ACAV-2 capillary viscometer using a set of glass capillaries was used to determine ultra-high shear viscosity. The shear rate ranges associated with these various viscosity measurements and what they apply to are shown in Table III.

The Anton-Paar instrument was used with the dynamic viscosity attachment to determine the rate of dewatering of the coatings. Static water retention was measured using an AA-GWR.

Table III: Shear rate ranges for various viscosity measurement systems and the environment they can apply to.

Environment	Method
Low shear, mixing	Brookfield ($<1000 \text{ s}^{-1}$), Cone-Plate ($<3000 \text{ s}^{-1}$)
Moderate shear, pumping	Hercules ($4\text{-}6 \times 10^4 \text{ s}^{-1}$), Cone-Plate ($1\text{-}2 \times 10^4 \text{ s}^{-1}$)
High shear	Capillary (10^6 s^{-1})
Elastic/Elongational	Cone-Plate, other

RESULTS AND DISCUSSION

The 20 and 100 rpm Brookfield viscosities are plotted as a function of solids for the formulations grouped as outlined previously in Figures 3 and 4. For the 100 parts and 50:50 blends of FGCC with the kaolin pigments in the 8 latex and 8 low molecular weight starch formulations it appears that the solids is the main driver for what the viscosities were for both low shear shear rates on the Brookfield. Possibly at 20 rpm the FGCC is on a separate curve from all the kaolin pigments. The changes in binder created dramatic differences in the Brookfield even at the same solids. This is as would be expected. For the high molecular weight starch the viscosities could be lying on the same line whether at 4 parts or 8 parts in the formulation. At low shear rates generally the solids, fines content and viscosity of the medium the particles are suspended in are major drivers of the measured viscosities. High fines content suspensions under low shear tend to be softly agglomerated. As the shear rate increases then these soft agglomerates break down and the viscosity becomes lower. We will see that at much higher shear rates the measured viscosities will be lower and influenced more by the solids content and the viscosity of the medium (starch molecular weight and amounts).

Just by comparing the 20 rpm to 100 rpm Brookfield results shows how shear thinning these coatings can be. The viscosities in Figure 4 are much lower than in Figure 3, but some of the same relationships can be seen of the influences of solids and the viscosity of the medium the pigments are suspended in.

Figure 5 shows the results for the apparent viscosity as measured by a Hercules viscometer at 4400 rpm using an E Bob. At this much higher shear rate of $46,288 \text{ s}^{-1}$ there is more differentiation between the various pigments in the 100% pigment formulations. Upon blending the various kaolin shapes and sizes with the fine GCC pigment the coating formulation viscosity measurements again appear to be more solids dependent like the Brookfield measurements for the platy kaolin pigments. The more traditional fine and delaminated kaolin pigments appear to lie on separate lines from the platy clay data. The effect of the viscosity of the medium as affected by the molecular weight and level of the starch is again evident. The effect of the starch level and molecular weight also causes a dramatic change in the viscosities at the high shear rates of this measurement. In the Imerys laboratory the general experience is that a coating formulation that has a higher than 75 mPas viscosity level will not run on a CLC-2000 laboratory coater without exhibiting banding, spitting and scratching. This is generally not a far different experience from discussions with mill personnel on their blade coaters. The higher molecular weight starch containing coatings and the highest solids coatings whether they were the platier or blockier kaolin pigments tended to be at this level or above. They were not applied using the CLC-2000, but it would be expected that they would not run well.

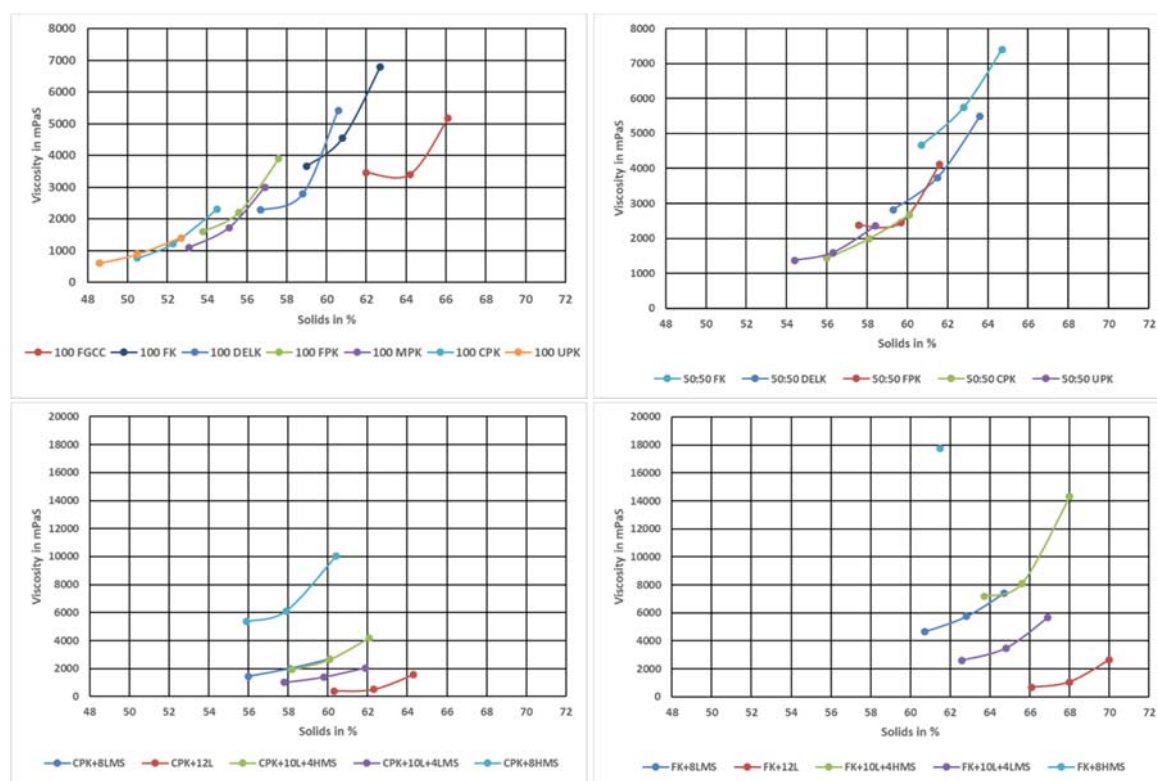


Figure 3: Brookfield results at 20 rpm ($\sim 10 \text{ s}^{-1}$ shear rate) as a function of coating solids.

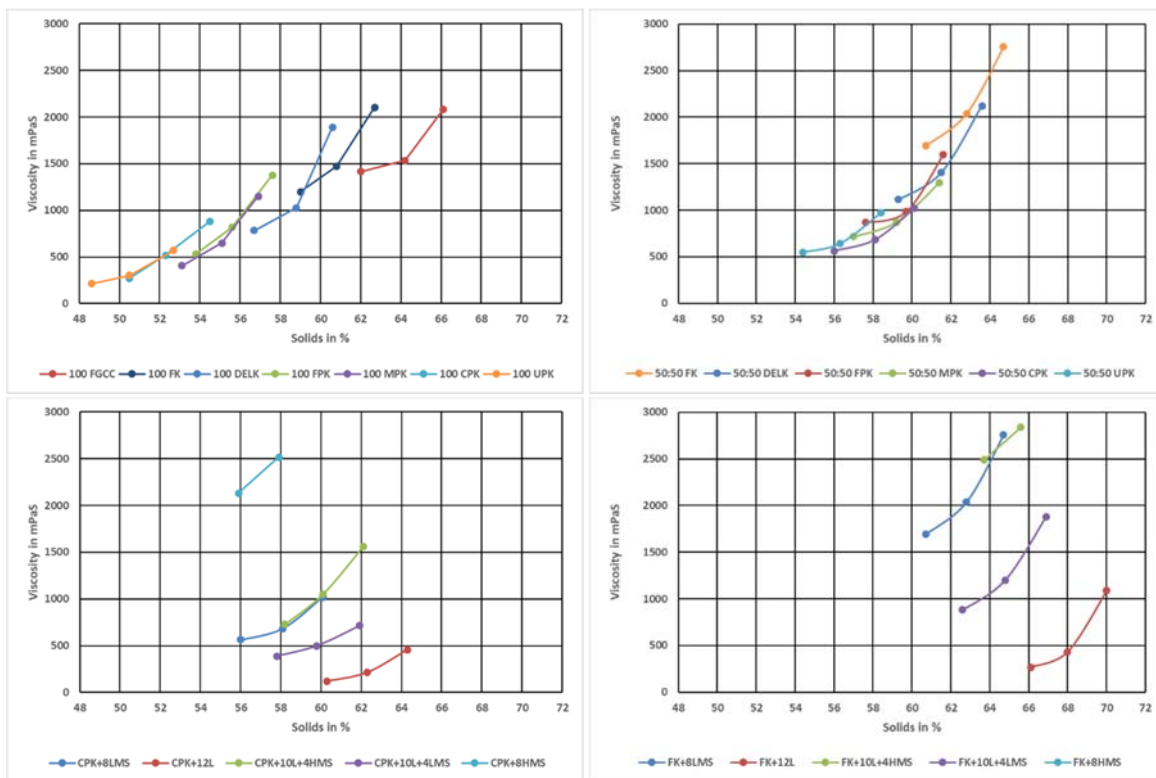


Figure 4: Brookfield results at 100 rpm ($\sim 30 \text{ s}^{-1}$ shear rate) as a function of coating solids. Higher shear leads to lower viscosities, but the relative differences are similar to the 20 rpm results.

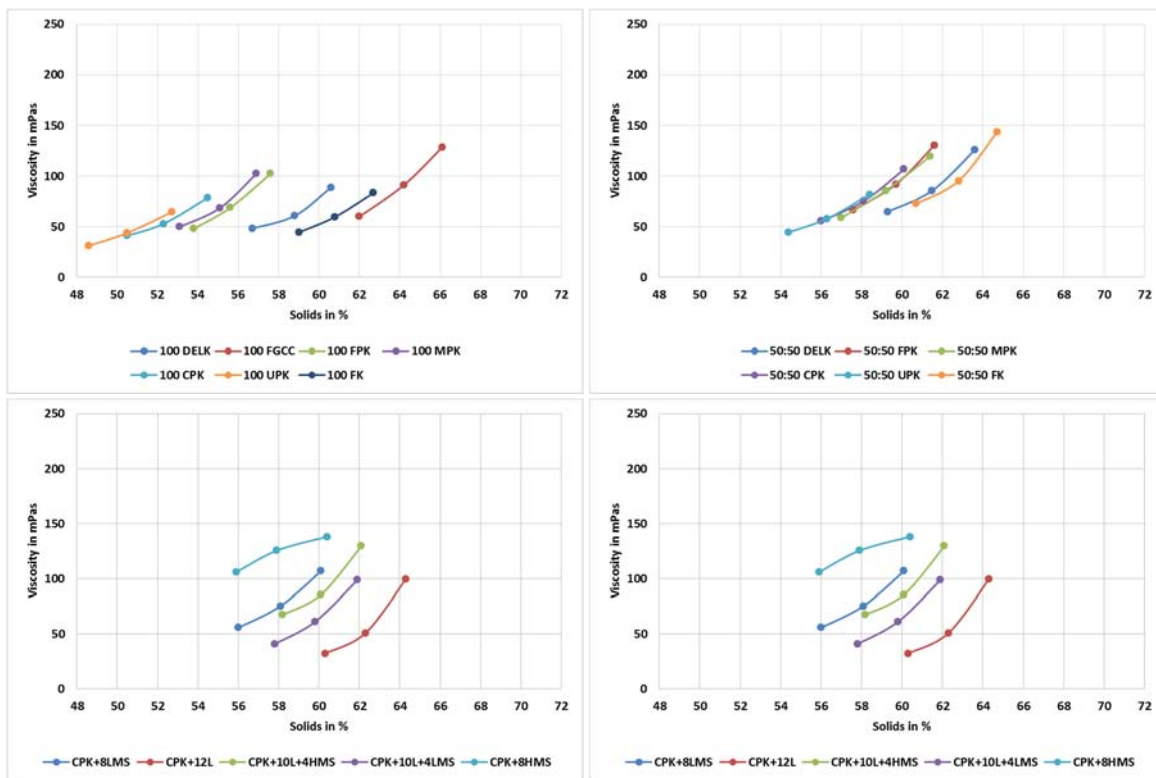


Figure 5: Hercules results plotted as a function of coating solids.

Figure 6 shows the viscosity versus solids results for measurements of the coating viscosities using an ACAV-2 capillary viscometer. Only the 100% pigment and 50:50 blends of the kaolin pigments with the GCC are shown. Much like the Hercules there is some separation of the pigments from each other for the 100% pigments. The blends however seem to indicate that the solids rather than just the shape is a major driver of what the viscosity is. This is as opposed to the 100% pigment results where shape is causing a separation of the curves. However, it must be kept in mind that particle shape is what is causing the differences in the solids in the first place.

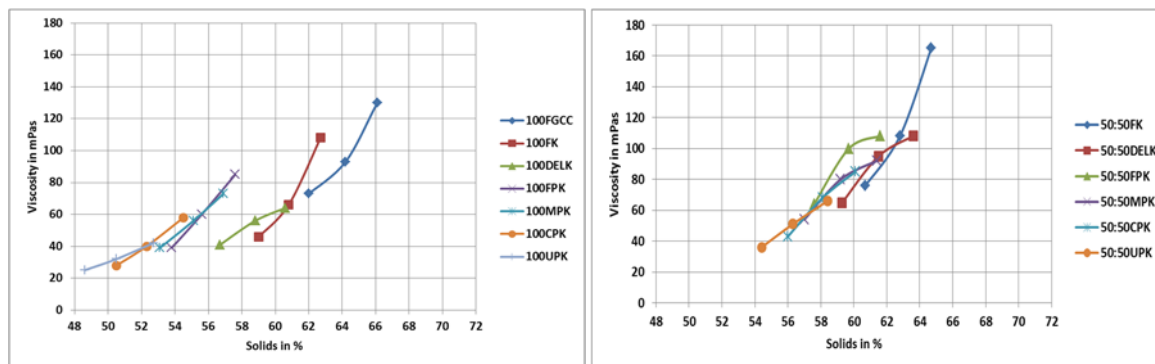


Figure 6: Viscosity measured at $500,000 \text{ s}^{-1}$ with an ACAV-2 Capillary Viscometer as a function of solids.

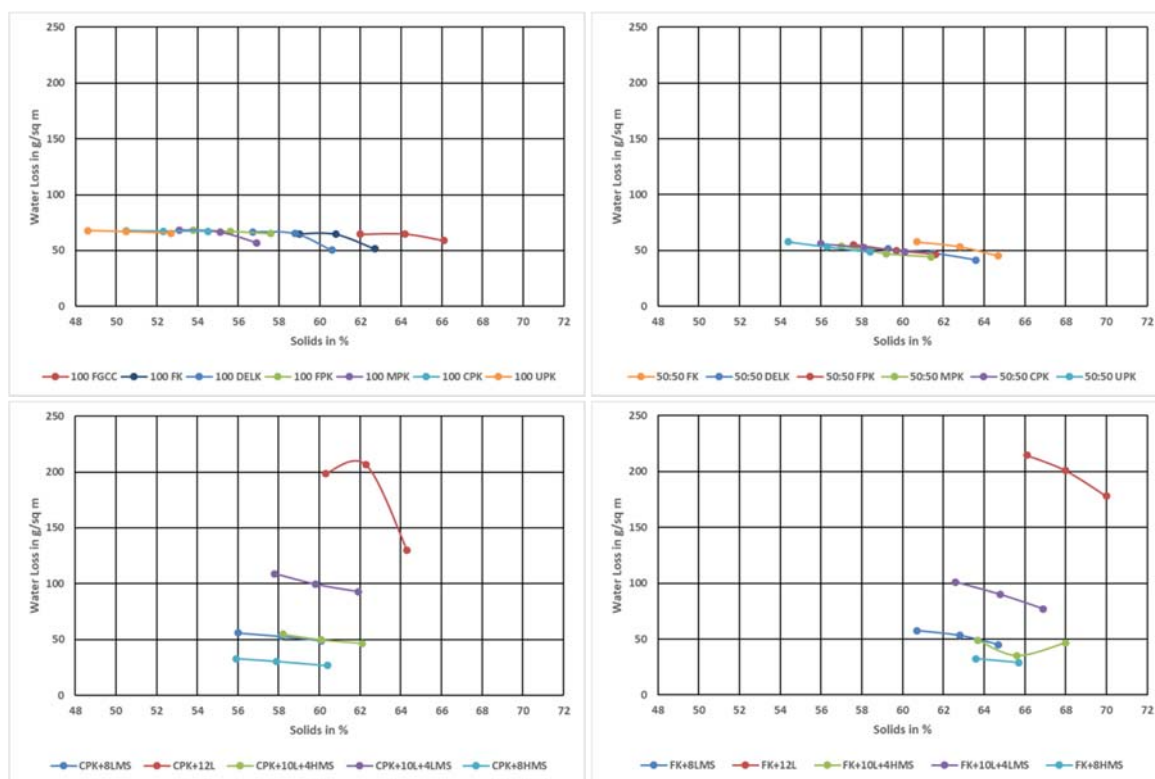


Figure 7: AAGWR results as a function of coating solids.

The static water retention results as measured with the AA-GWR are shown in Figure 7. Interestingly for the 100% pigment coatings there is very little difference between the pigments. That is even while considering the pretty wide coating solids differences. Same story applies to the 50:50 blends of pigment coatings. Where there are large

differences for the changes in starch molecular weight and level. With higher levels of starch and an increase in molecular weight the water retention increases as would be expected.

The viscosity as a function of coating solids at a shear rate of 1000 1/s is shown in Figure 8 as measured with an Anton-Paar cone and plate viscometer. For the 100% pigment and 50:50 blend coatings the major influence on the viscosity at constant levels of starch and latex are mostly the level of solids. As we change the binder system we see dramatic changes in the viscosity. These results across the shear rate range measured (10 to 1400 1/s) will be used to obtain the Ostwald-de Waele power law parameters for the 100% pigments and the 50:50 blends.

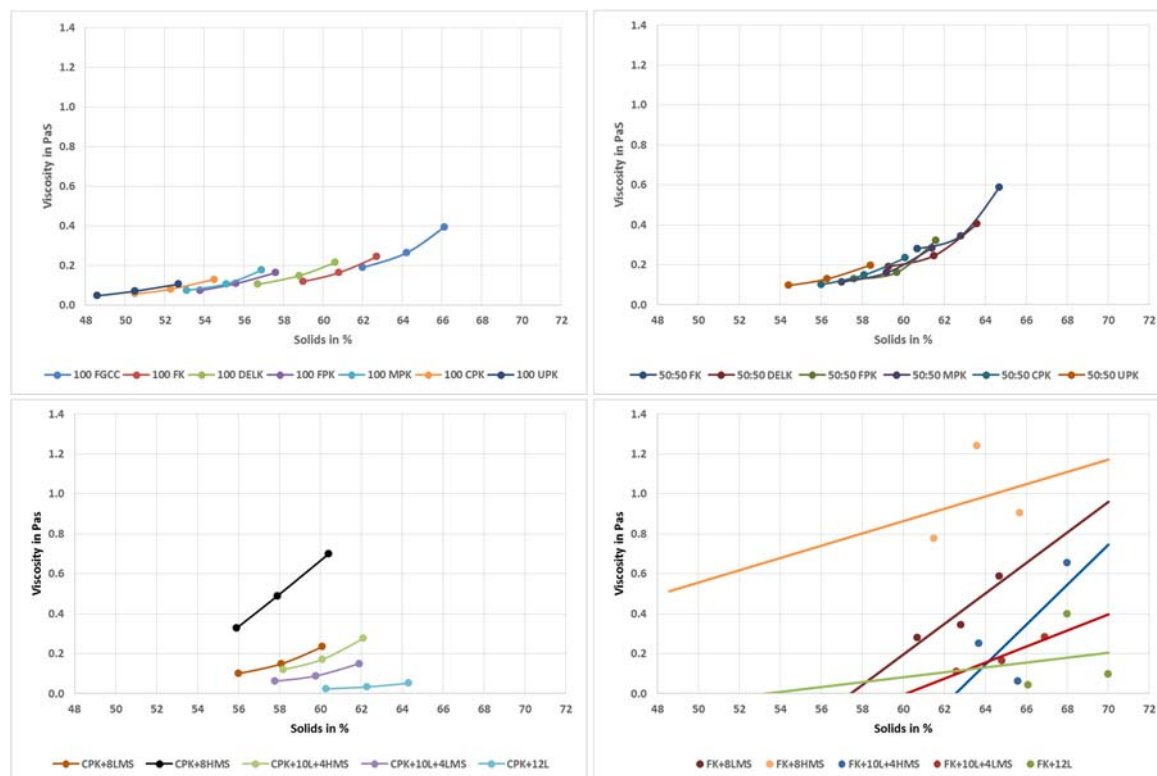


Figure 8: Cone and plate viscosity at 1000 s⁻¹ shear rate as a function of coating solids. The fine kaolin results where the molecular weight and level of starch was varied was not well behaved and so linear trend lines were fit to that set of data instead of the spline fit used for the rest of the data.

The dynamic dewatering results are plotted in Figure 9. They indicate for the 100% pigments that the dewatering rate does not change much as a function of the solids or of the shape of the particles. It is surprising that even though there are large differences in the solids between the various pigments that the dewatering rates do not change much. The 50:50 blends generally show a similar result. The one exception is that the dewatering rate of the fine blocky kaolin with GCC seems to have a slower dewatering rate. There were some issues in measuring the formulations with binder changes and so unfortunately conclusions are difficult to make. It was expected that the higher molecular weight and higher starch containing formulations would have had a slower dewatering rate. One can safely conclude that the formulation with only latex as the binder had a faster dewatering rate than those that contained starch.

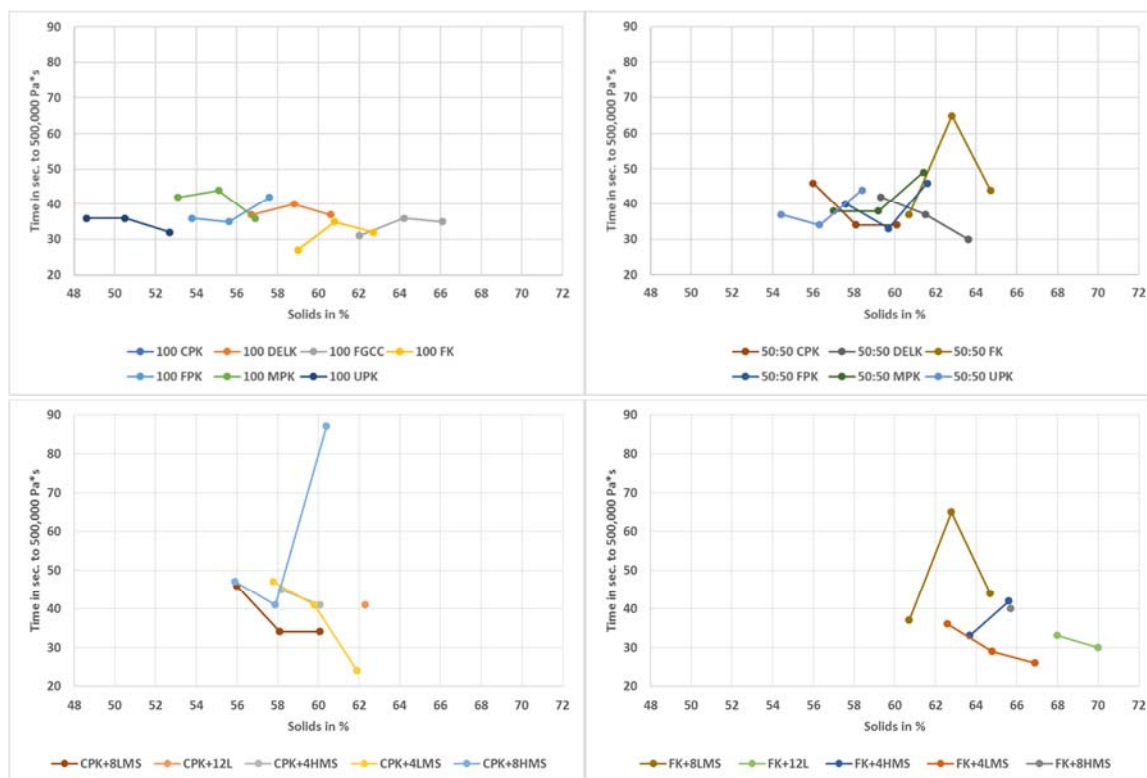


Figure 9: Dynamic dewatering of the formulations using the BASF apparatus. Time to 500,000 Pa*s is plotted as a function of solids.

The viscoelastic behavior of the coatings was quite surprising. The oscillation results are plotted in Figure 10. $\tan \delta$ at 1.1 Hz is plotted as a function of coating solids as was the other properties. $\tan \delta$ is the ratio of the viscous to the elastic modulus. For the constant binder systems this ratio looks to be a function of the solids and not necessarily of the particle shape. This was true for the 100% of the pigment formulations and the 50:50 blends. As the solids increases the coating formulations become more elastic or solid like in behavior rather than as a viscous fluid. The blockier pigments were much more elastic in behavior than the platier pigments were. Also as the level of starch or the molecular weight is increased the 100% FK and CPK formulations becomes more elastic solid in behavior. The formulations without starch and only latex binder had very viscous fluid behavior. A hypothesis that needs to be verified by further experimentation can be formed that the weeping and whiskering that is often observed for platy pigments might be caused by the steep response of $\tan \delta$ as the solids of the coating formulation changes. The platier pigments had the higher viscous component in comparison to the blockier ones, but also had a steep response to changes in the solids. Is this purely driven by the solids or the flow behavior of aligned plates as well?

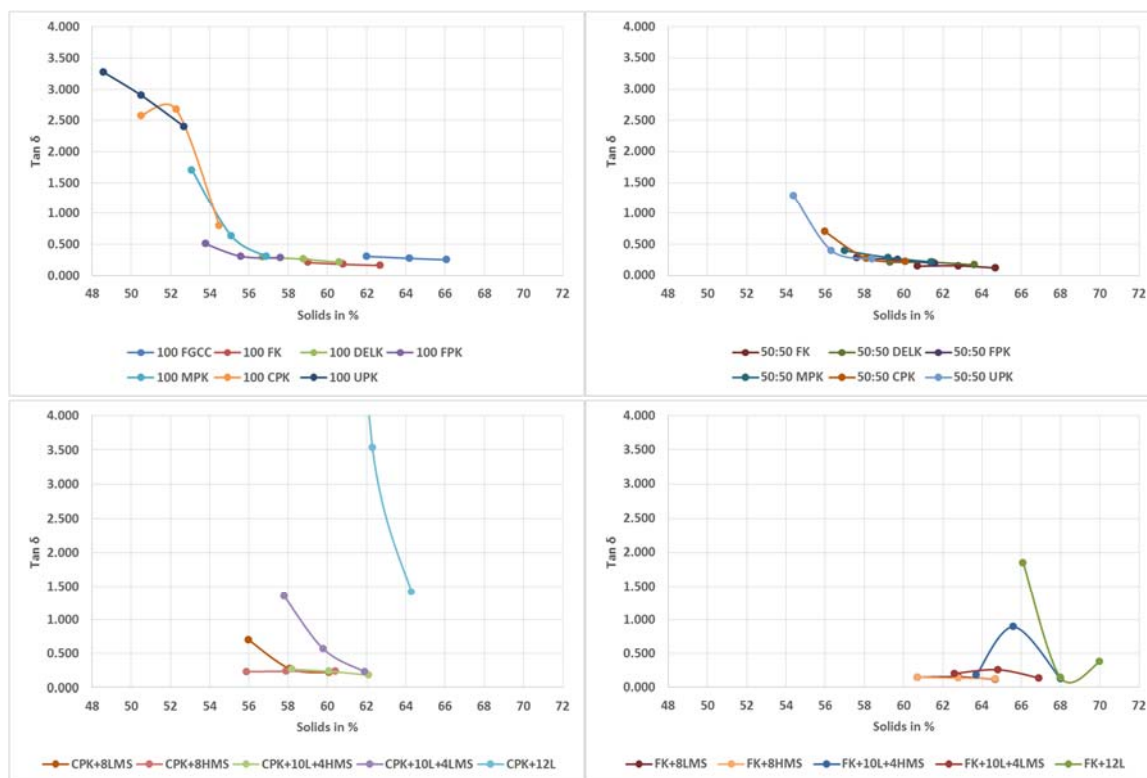


Figure 10: Oscillation results with cone and plate configuration at 1.1 Hertz oscillation. $\tan \delta$ (viscous modulus/elastic modulus) is plotted as a function of solids.

CALCULATION OF THE OSTWALD-DE WAELE POWER LAW PARAMETERS

The Anton-Paar cone and plate shear results were used to determine the Ostwald-de Waele (2-5) power law parameters, where $\mu = \mu_{FC} \dot{\gamma}^{(n-1)}$, for the 50:50 blends. In the power law μ is the viscosity, $\dot{\gamma}$ is the shear rate, n is the power law index, and μ_{FC} is the flow consistency. Excel's power function trend line data fit was used to determine μ_{FC} and n in the constitutive equation. Table IV is a summary of the results for the various 50:50 blend coatings.

Figure 11 shows data for the 50:50 blend of MPK and FGCC for the cone and plate data. In Figure 11 the power law trend line fit is also shown for each solids level. As might be expected the μ_{FC} parameter dramatically changes as the solids changes. It also appears that the shape factor is the main effect on n .

The n index is plotted as a function of the shape factor of the kaolin pigment in the coatings in Figure 12. As the shape factor of the kaolin in each blend increases the coating becomes more shear thickening. However, n remains less than 1 for all of the coatings and so all of them are shear thinning. The degree to which they are shear thinning is all that is changing. The result for the n index seems to fit well to a second order polynomial.

Table IV: Summarized results for the 50:50 blend coatings for the n index and flow consistency and the relevant properties of the pigments.

	Solids	Shape Factor	μ_{FC}	n
50:50 FK	64.7	14	54805	0.342
	62.8	14	35276	0.325
	60.7	14	27793	0.331
50:50 DELK	63.6	35	27878	0.38
	61.5	35	16043	0.388
	59.3	35	12495	0.391
50:50 FPK	61.6	58	13691	0.448
	59.7	58	5039.2	0.494
	57.6	58	4691.2	0.471
50:50 MPK	61.4	77	8843.2	0.492
	59.2	77	5138.9	0.488
	57	77	3832.7	0.481
50:50 CPK	60.1	83	7550.4	0.485
	58.1	83	4007.2	0.513
	56	83	2681	0.515
50:50 UPK	58.4	97	5835.7	0.502
	56.3	97	4544.5	0.476
	54.4	97	2652	0.514

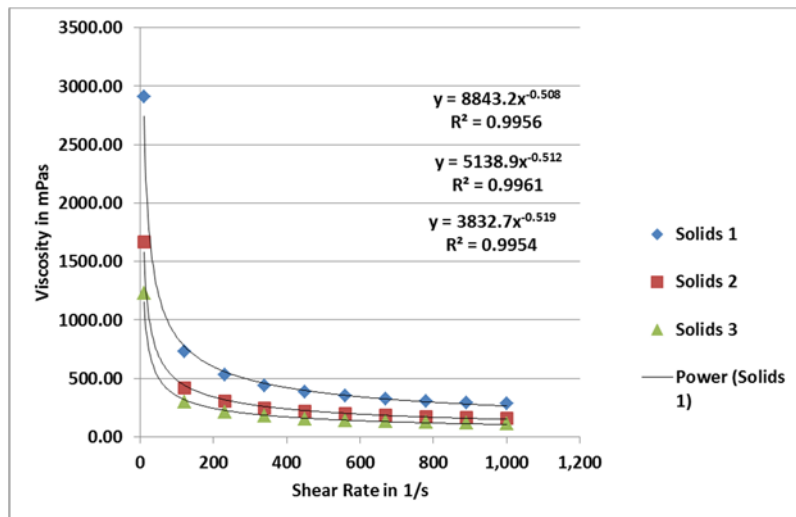


Figure 11: Example of the fitting done to the cone and plate data for the 50:50 MPK and FGCC coating at each solids level.

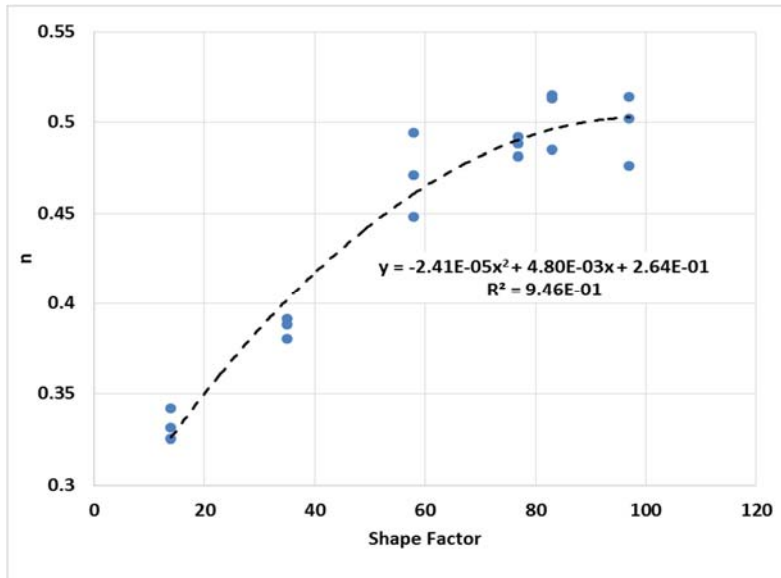


Figure 12: Plot of n versus the shape factor of the kaolin portion. The higher that n is the more shear thickening the coating is.

Figure 13 shows the strong relationship between μ_{FC} and the coating solids. This parameter can be fit to a third order polynomial as a function of solids. The R^2 is a bit on the low side at 0.855. Both results show the strong influence of the kaolin shape factor on the rheological properties as well as the effect of the solids.

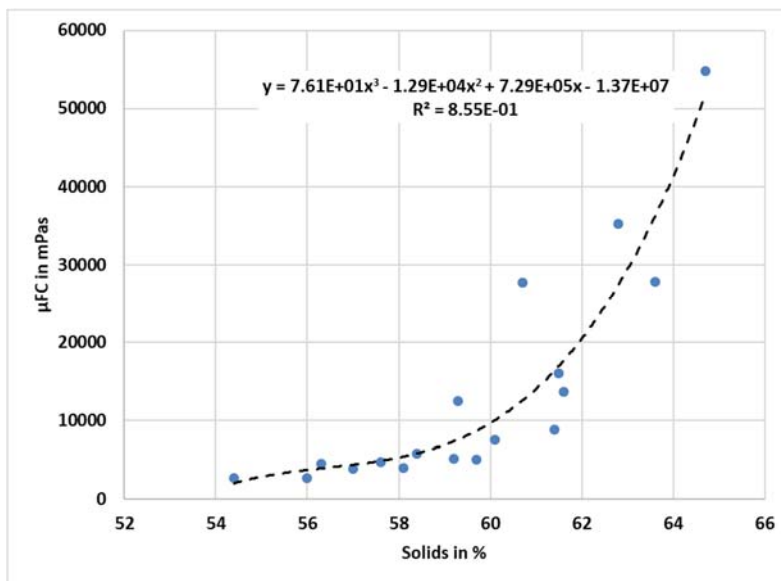


Figure 13: μ_{FC} as a function of solids for the various 50:50 blend coatings.

DOUGHERTY-KRIEGER AND THE WEEKS ΔS

As previously discussed, the difference between the immobilization solids and the coating solids is important to how well a coating will run on a blade coater and possibly at the metering point on a rod coater. Since three solids were run for each coating, we have enough data to calculate the immobilization solids. This was applied to the 100% pigment and the 50:50 coatings.

The α parameter should be related to the shape of the particles and indeed we see the influence of the shape. This is particularly true for the 100% pigments where the blockier pigments are in a range from 4.3 to 5.5 and the platier ones are in a range from 7.0 to 7.7. Then with the blends we get a narrower range for α where they are in a range from 4.1 to 4.9. Likely this is directly to do with the blockier component in the blend diluting the shape of the population of particles. There also may be some synergistic effect that will be investigated in the next section.

The immobilization or max solids calculated here can be plotted versus the shape factor. It was expected that there should be a relationship between the immobilization solids and the shape of the particles and this is clearly shown in Figure 14.

The immobilization point of the coating is also affected by the 0.25 micron content of the particle population where the higher it is the lower the viscosity at high shear should be. This is demonstrated in Figure 15.

Table V: Results from the calculation of the parameters in the Dougherty-Krieger equation for the 100% pigment and 50:50 blend coatings with 8 parts of the low molecular weight starch.

	Max Solids	μ_0	α
FGCC	79.1	2.13	5.3
FK	76.9	1.76	5.5
DELK	74.4	4.37	4.3
FPK	71.5	1.35	7.1
MPK	70.4	1.41	7.0
CPK	70.0	1.80	7.0
UPK	68.7	1.26	7.7
50:50 FK	76.2	3.00	4.9
50:50 DELK	76.3	3.60	4.8
50:50 FPK	71.5	4.42	4.5
50:50 MPK	71.1	5.24	4.1
50:50 CPK	69.9	4.40	4.4
50:50 UPK	69.4	3.56	4.7

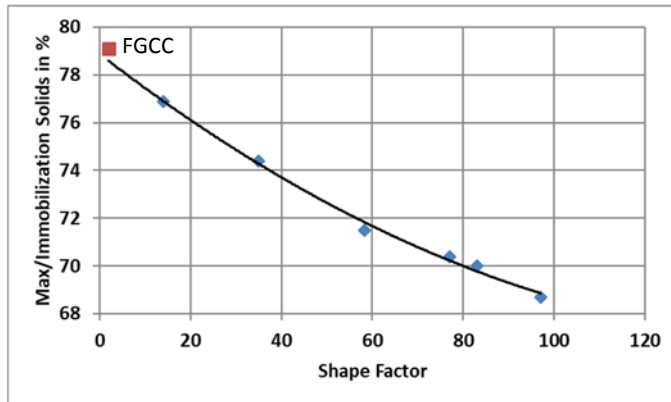


Figure 14: The maximum or immobilization solids as a function of the shape factor for the 100% pigment coatings.

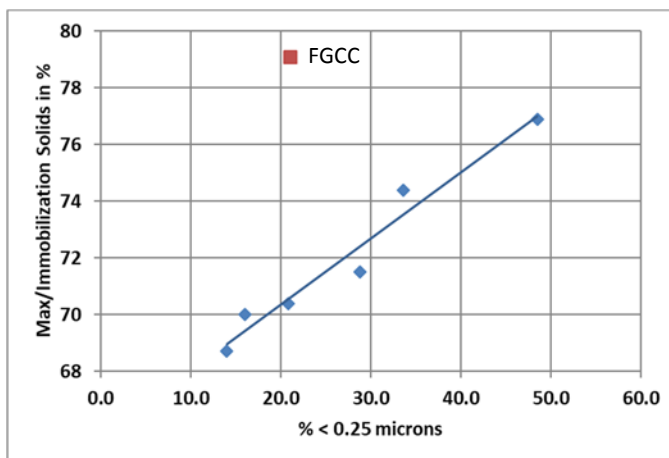


Figure 15: The immobilization solids increases as the 0.25 micron content increases for the 100% pigment coatings. The very blocky carbonate is off the curve.

In the 50:50 blend coatings the 0.25 micron content of the kaolin portion of the blend and shape factor still influences the immobilization point quite strongly. The immobilization solids are plotted versus the shape factor and 0.25-micron content of the kaolin portion of the coatings in Figure 16.

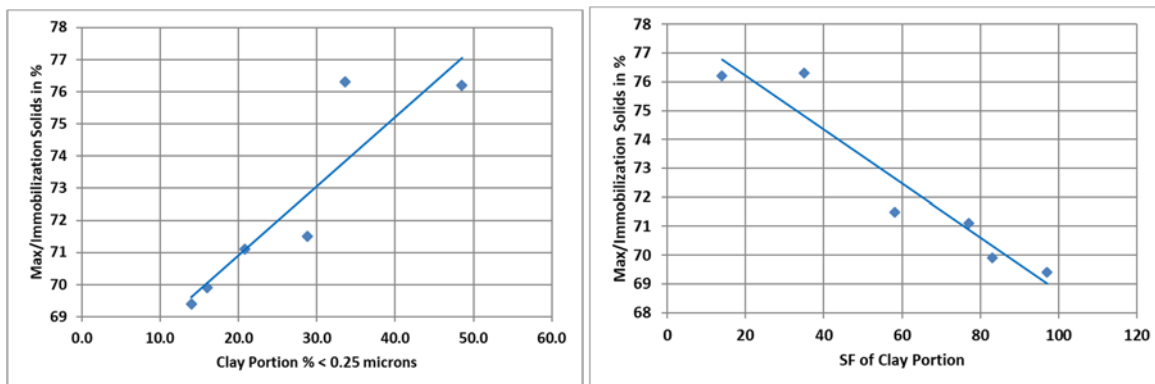


Figure 16: The strong influence of the kaolin portion characteristics in the 50:50 blends on the immobilization solids.

Utilizing this method to determine the immobilization solids allows one to then project for their coater and base sheet what solids to run with a new formulation. Simply use the current ΔS to calculate the solids that the new coating needs to be run at using the new immobilization solids. As an example, if the 50:50 FK coating is currently running well at 62% solids then the target ΔS would be 76.2 minus 62 or 14.2. If there is a switch to the 50:50 FPK formulation, then the new coating would need to be run at 71.5 minus 14.2 or 57.3% solids. All of this assumes that no other changes are made to adjust the water-holding of the coating.

DOUGHERTY-KRIEGER AND SYNERGY

It appears that there is some relationship between the shape factor of the kaolin portion of the 50:50 coatings and α and μ_0 . These two parameters are plotted versus the shape factor in Figure 17. That a parameter like α would be related to the shape of the particles makes some sense. This parameter is in the denominator and so as it gets smaller so does the denominator making the viscosity higher. In addition, from Einstein's theory it is expected that α will change with particle shape. In much the same mathematical way the μ_0 parameter maximizing at the most structured point makes sense. However, since this parameter is supposed to be related to the suspending fluid it requires more thought. Is it possible that the colloidal fraction that is less than 0.25-micron in size has some influence on this parameter? Possibly it is minimized at this point so that the high shear behavior as measured by the Hercules is affected? The viscoelastic measurements seemed to indicate that the viscous nature of the coating increases as the shape factor of the kaolin increases. Is this more evidence to this behavior?

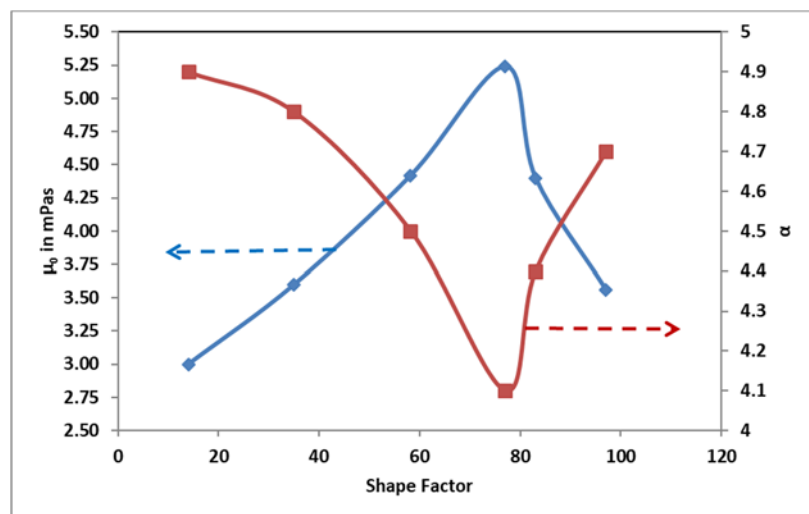


Figure 17: When μ_0 and α are plotted as a function of the shape factor a minimum in α and maximum in μ_0 emerge indicating an optimum in structuring synergy between the kaolin and GCC in the coating at around a kaolin shape factor of 78.

SUMMARY AND CONCLUSIONS

The solids of a coating strongly dictate the rheological characteristics of a coating. As the shape factor of the kaolin that is used increases the solids must shift downwards. This is true for the low shear, high shear, and viscoelastic properties of a coating. Surprisingly even though the solids of a platier kaolin containing coating are much lower than its blockier counterpart coatings the water-holding characteristic doesn't change very much. The effect of the

binder can be quite profound. Changes in level of soluble polymers like starch or the molecular weight has a profound effect on all of the properties of the rheological properties of the coating. The use of a high molecular weight starch can make platy kaolin containing coatings difficult to impossible to run on a blade coater.

Platy kaolin containing coatings tend to have a high viscous component in comparison to blocky kaolin and carbonate pigments. Does this mean that more elastic or solid like behavior around the coater is preferred over a more viscous dominated behavior? Is this why high molecular weight starch containing coatings do not run well especially with platy kaolin? These questions may need further investigation.

It was demonstrated that all coatings in this study are shear thinning. The Ostwald-de Waele Power Law model was used to model this shear thinning behavior. The degree of shear thinning is all that changed from coating to coating.

The immobilization point of a coating can be determined using the Dougherty-Krieger equation and using viscosity measurements at three solids levels or more. A technique is demonstrated on how to calculate where to target solids as pigment changes are made without changes in the binders and other additives using the Weeks ΔS method. It was also demonstrated how the shape factor of the kaolin pigment effect the immobilization point of a coating. A methodology is demonstrated here that deserves more investigation on the use of the Dougherty-Krieger technique to demonstrate synergies between various pigments in terms of maximization of the bulk or porosity of the coating as indicated by a minimum in a plot of the inherent viscosity α as a function of the shape factor of the kaolin component in blends with a fine carbonate. There was also a maximum in the media viscosity μ_0 plotted as a function of the kaolin component in blends with a fine carbonate.

ACKNOWLEDGEMENTS AND DEDICATION

I would like to thank Perry Veal and Lisa Buttitta at the Imerys Technical Service Laboratory in Sandersville for generating this data set for me. This paper and presentation is dedicated to the memory of David Cummings who was Perry's and Lisa's supervisor when this work was done. David provided his excellent guidance and training in facilitating getting this enormous data set generated. David's unfortunate passing has taught me to be even more aware of bicycle riders while driving.

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