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The Effect of Calcium Carbonate in the Coating Color on Gloss

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THE EFFECT OF CALCIUM CARBONATE
IN THE COATING COLOR
ON GLOSS

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ABSTRACT

This thesis involved the study of the effects of calcium carbonate on gloss. The variables investigated were different types and levels of calcium carbonate in the coating color. Four different calcium carbonates, three ground and one precipitated, were used. The calcium carbonate/clay ratio changed from 0% carbonate/100% clay to 75% carbonate/25% clay in increments of 25. The coat weight target was 12 +/- 1 g/m2. The coating colors containing higher levels of calcium carbonate had better low shear viscosities; therefore, these coatings were able to run at the 62% solids target.

It was found that calcium carbonate decreases gloss in comparison to the 100% clay coating, and the larger the particle size of the CaCO3 the greater the decrease. However, the coarsest calcium carbonate (GCC-60) did produce the greatest gains in gloss after supercalendering. The GCC-Hg which had the smallest average particle size did not significantly change the gloss at higher substitution levels. The GCC-90 had no significant effect on gloss until the 75% substitution level, when a decrease occurred.

The narrow particle size distribution of the PCC was detrimental to gloss, and it was also a factor in the brightness loss due to Ink absorption.

The brightness loss of the coatings due to K&N ink absorption corresponded to the gloss results, except for the PCC trend. PCC had the most dramatic decrease in brightness.

INTRODUCTION

The use of calcium carbonate in the American paper industry has dramatically increased since the late 1980's, following the increase in alkaline papermaking. Calcium carbonate in the coating color has been found to have many advantages compared to clay. These are: higher brightness, improved rheology, binder savings, better printability, and energy savings. The disadvantage is reduced gloss.

This paper is a contribution toward an improved understanding of the role of calcium carbonates in the coating color on gloss. Gloss is a measure of the ability of a coated paper to reflect light specularly. Achieving higher levels of gloss may be considered as one of the most important properties of coatings as it is characteristic of high quality coated papers.

The objective of my research was to observe the effect of varying levels and types of calcium carbonates in the coating color on gloss. The background and literature review section of this paper review the factors considered most important to gloss development, when considering the pigment portion of the coating color. These are the pigment particle size, shape, and orientation, as well as coat weight, and the finishing condition.

THEORETICAL AND BACKGROUND DISCUSSION

Theories of Gloss Development

Gloss is a measure of the ability of a coated surface to reflect light specularly. The Fresnal Theory states that the specular reflection of light on an optically smooth surface is a function of its refractive index and angle of incidence. Chanmayanandam's theory for the specular reflectance of a rough surface states that specular reflectance is a function of the angle and wavelength of incident light as well as roughness(1). T.A.P.P.I. gloss is determined by the refractive indexes and surface roughness. The refractive indexes for most coating additives are similar except that of TiO_2, therefore the differences in gloss of most coatings are due primarily to surface roughness, and a high coating gloss can be achieved if the surface is microscopically smooth, but macroscopically rough. Gate (2) showed in his study that surface microtexture has a significant effect on the measurement of gloss since the peaks and valleys in a surface profile are a significant fraction of the wavelength of light used, and this effects how light reflects from the surfaces. The factors contributing to gloss development or surface microtexture in the coating color are pigment particle size, particle shape, particle orientation, the type and quantity of adhesive used, adhesive movement, smoothness of the base sheet, degree of coverage of the base sheet and the finishing conditions. In the following sections the effect of particle size, shape, and orientation, coat weight and finishing conditions on the surface microtexture are discussed.

Particle Size

The optical properties brightness, opacity, and gloss are all strongly affected by the particle size of the pigments used in the coating color. Zeller(3) states that the optimum particle size for light scattering is usually 0.2-0.8 um for calcium carbonate pigments, but the exact optimum size for good optical properties is uncertain. One reason for the uncertainty is that the optical properties of paper coatings depend on factors, such as pigment loading level, degree of dispersion and coating composition. For example, the optimum particle size at a high pigment loading level is not necessarily the optimum particle size at a low level. Also, the effective particle size is affected by the degree of dispersion; the agglomeration of several fine particles may act like a single coarse particle(3).

The average particle size of calcium carbonate pigments affects its pigment volume concentration(PVC) which is correlated to gloss development by Zeller(3). He graphed PVC vs. Gloss at a variety of average particle sizes. He determined a U-shaped dependence of gloss on PVC for all particle sizes. This was not expected because both the latex binder by itself and the calcium carbonate pigment at high PVC have high gloss values. Zeller(3) suggests at intermediate PVC's the pigment particles interfere with the coalescence of the latex particles, and thus prevent the formation of a smooth film which is necessary for high gloss.

Zeller(3) stated that gloss is strongly affected by the PVC and particle size; the highest gloss was produced by fine particles and high PVC.

The effect of clay particle size on coating structure was studied by Kraske(4). He determined that the unbound surface area of the coating increased substantially as the particle size of the clay was decreased. He observed the orientation of the clay platelets and showed that as the particle size decreased the orientation increased. He believed that the larger particles were more difficult to align before being immobilized during drying. The pore size and void volume also increased as the particle size increased, allowing for more refraction instead of reflection. Trader(5) showed that gloss increased linearly with decreasing particle size of clay.

The effect of particle size distribution to surface roughness is stated by Lee(6), anything that decreases surface roughness will increase gloss. Therefore, as you go to smaller particle sizes, packing efficiency increases because void spaces are filled, thereby decreasing surface roughness and increasing gloss.

Particle Shape

The particle shape of the coating color pigments is strongly believed to influence pigment performance. Particle shape influences particle packing, slip, coating color rheology, and coated paper properties such as pick resistance, opacity, gloss, and ink absorption(7).

The particle shape of clay is a platelet, ground calcium carbonate is a rhombohedral and the precipitated calcium carbonate can be found in a variety of shapes. Crawshaw(7) found in his study that the coated paper property most influenced by particle shape is gloss. He found that the major effect of shape is upon particle packing. Crawshaw(7) states that the addition of PCC disrupts the dense packing of the clay platelets. It also interferes with the orientation of the platelets that should lie parallel to the paper surface to optimize gloss. Good particle packing will decrease the voids and pores. Therefore, increasing the smoothness of the coated surface.

In the study conducted by Lepoutre(8) it was found that the introduction of spherical plastic pigment in sufficient amounts into a delaminated clay or sphere-like PCC produced a decrease in surface roughness and contribute to an improved gloss. He determined that gloss is a function of the manner in which the packing of the particles effect the smoothness of the surface.

Particle Orientation

The theory that gloss is a result of the surface particles oriented parallel to the plane of the sheet, accompanied by the flow of the binder to allow the motion has long been accepted. However, Lepoutre(8) found little or no correlation between particle orientation and gloss development in the supercalender. The gloss of the uncalendered coating may be a function of the degree of particle orientation, but gloss developed in the supercalender was not. Contrastingly, Van Gilder(9) believed that gloss increased after calendering due to the tendency of the clay platelets to flatten or orientate.

Coat Weight

It has been shown that gloss increases as coat weight increases. Lee(6) found that the gloss of calendered coated papers increased as coat weight increased, but leveled off as it approached the ultimate gloss for the system. At low coat weight the gloss of the coated paper is dependent upon the coat weight and the particular system, but at high coat weights, the gloss is independent of the system.

The coat weight interval where the greatest change in the rate of gloss development occurred was approximately 4 and 5 g/m2 (10). This is believed to be dependent on the critical pigment demand. Kraske(4) found that lighter coat weights have a lower degree of orientation than heavier coat weights. This results because the vehicle drains from the light weight coating into the raw stock and immobilizes the clay platelets before they have an opportunity to orientate to the extent they do in heavier coatings.

Higher coat weights can be obtained when higher solids coatings are utilized. Huggenberger(11) found that coating gloss was improved as the coating solids were increased in a ground calcium carbonate/latex/CMC coating color. At the higher solids more uniform coverage of the fibers was obtained.

Finishing Conditions

Calendering increases the gloss exponentially so that it increases less with each additional nip(4). Gloss due to calendering is dependent on calender temperature, moisture content, and nip pressure.

Lepoutre(8) found that gloss increased with calendering pressure and the number of nips. At high pressures the kaolin plates are pressed into the coating, squeezing out the latex polymer which flows and fills out the depressions resulting in a decrease in microroughness and increased gloss. Increasing the number of nips increases the amount of time the pressure has to act upon the sheet.

Heat which is generated in the nips due to the high pressure and the external heat applied to the sheet help to deform the binders. As the temperature is increased the binder becomes more plastic and flows easier allowing the surface to be reoriented to increase smoothness.

Van Gilder(9) found that the first nip on the supercalender increased gloss of the high clay coatings to a much larger extent than that of the high carbonate coatings. He believed this was the result of the higher level of clay platelets, which had more of a tendency to flatten to a larger extent than that of the spherical-like calcium carbonate particles.

EXPERIMENTAL PROCEDURE

Experimental Design

The experimental design was structured to test the effect of calcium carbonate type and quantity on gloss. This was accomplished by preparing coating colors containing varying clay/carbonate ratios and equal amounts of latex binder, and polyphobe thickener. The initial solids target was 62 %.

The cylindrical laboratory coater (CLC) was used at 3500 ft/min to synthesize a high speed blade coater. The coat weight target was 12 +/- 1 g/m2. The coated paper was tested for gloss. The paper was then supercalendered at 1000 pli for 4 nips. The temperature of the supercalender rolls were 43.2 C (bottom roll) and 36.6 C (top roll). Following supercalendering the paper was tested for gloss and K&N ink holdout.

Coating Preparation

Hydragloss #1 ultrafine clay, 87-89 % brightness and 92-98% less than 2 um. was dispersed at 70% solids in the Cowles mixer. The ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) were received from suppliers in a slurry. See Table I for a physical description. A carboxylated styrene/butadiene latex at 48% solids and a polyphobe thickener at 25% solid were used. Table II shows the coating formulations.

The coating formulation ingredients were weighed out on the basis of 3000g dry solids/formulation and mixed mechanically. The order of addition was clay, calcium carbonate, latex, water, and polyphobe. The coating colors were tested for solids, Brookfield viscosity, and Hercules Hi-shear viscosity (See Table III). The target solids was 62% initially. However, solids were lowered on some formulas when runnability problems occurred (See Table III).

Coatings were applied to a 69 +/-1 g/m2 base sheet using the Cylindrical Laboratory Coater (CLC) at a speed of 3500 ft/min. The target coat weight was 12 +/- 1 g/m2 with two runs at each coat weight.

Table I: Typical Physical Properties of Calcium Carbonate

Property	GCC-HG	GCC-90	GCC-60	PCC
Median Particle Size,um	------	0.7	------	0.6
+325 Mesh Residue,%	------	0.005	0.005	<0.01
Brightness,%	92	96	96	97
Surface Area,m2/gm	------	12	6	10
Slurry Solids,%	76	76	75	70
Fineness,% - 2 um	------	90	60	94
- 1 um	90	70	35	85

Table II: Coating Formulations

Coating Color	Run		
	#1	#2	#3
GCC-60	25	50	75
#1 Clay	75	50	25
Latex	15	15	15
Polyphobe	0.5	0.5	0.5
	#4	#5	#6
GCC-90	25	50	75
#1 Clay	75	50	25
Latex	15	15	15
Polyphobe	0.5	0.5	0.5
	#7	#8	#9
GCC-HG	25	50	75
#1 Clay	75	50	25
Latex	15	15	15
Polyphobe	0.5	0.5	0.5
	#10	#11	#12
PCC	25	50	75
#1 Clay	75	50	25
Latex	15	15	15
Polyphobe	0.5	0.5	0.5
	#13		
#1 Clay	100		
Latex	15		
Polyphobe	0.5		

Table III: Brookfield Viscosities and % Solids

Run #	Pigment Ratio	Viscosity (cP)	%Solids
	(GCC/Clay)	100 rpm	
1	25/75	8810	61.64
1A	"	1772	58.03
2	50/50	3248	61.65
2A	"	2164	59.70
3	75/25	1996	61.97
4	25/75	6000	61.89
4A	"	2464	60.17
4B	"	1756	58.12
5	50/50	1854	61.85
6	75/25	1960	61.68
7	25/75	8210	61.6
7A	"	1388	58.20
8	50/50	2940	61.91
9	75/25	2508	62.07
	(PCC/Clay)		
10	25/75	13600	62.03
10A	"	3012	56.16
10B	"	1368	53.61
11	50/50	7220	61.94
11A	"	6970	60.19
11B	"	4470	57.76
12	75/25	5540	61.89
12A	"	2948	59.39
	(Clay)		
13	100	1076	62.49

Supercalendering

The supercalender was preheated using radiant electric heating coils for six hours to reach a temperature equilibrium and loaded at 1000 pli. The temperature of the top roll was 36.6 C and the bottom roll was 43.2 C. The paper was conditioned at standard temperature and humidity and then supercalendered for four nips.

Evaluation Procedure

Coat weight was determined by measuring the basis weight difference before and after the coating application. The coated paper was tested according to TAPPI standard methods. Brightness, opacity, and gloss(75) were tested before and after supercalendering. Porosity, roughness, and K&N ink holdout were tested after supercalendering.

The Hunter Glossmeter was used to determine the gloss. The glossmeter is sensitive to surface variations on the scale of 0.02 um. Gloss is measured in the machine direction and the cross direction. The differences are due to the method of application of the coating. I am referring to an average of the machine and cross direction values in this discussion.

RESULTS

Table IV: Testing Results - Before Supercalendering

Run #	Gloss,% (MD+CD)/2	Gloss MD St.Dev.
1	20.1	1.16
2	12.2	1.20
3	8.1	0.49
4	26.8	1.34
5	22.6	2.14
6	17.2	1.28
7	26.8	1.55
8	28.3	2.35
9	25.8	1.12
10	22.1	2.12
11	18.1	1.75
12	15.3	1.61
13	27.3	2.21

Table V: Testing Results - After Supercalendering

Run #	Gloss,% (MD+CD)/2	Gloss MD St.Dev.
1	56.6	2.66
2	42.6	5.38
3	37.1	1.95
4	65.1	1.98
5	57.2	4.46
6	51	2.25
7	61.1	2.42
8	58.9	2.47
9	56.2	2.23
10	64.7	3.61
11	56.9	1.89
12	48.1	5.02
13	62.9	2.61

Run #	K&N,% Brightness	Delta Gloss,%
1	15.67	64.4
2	18.23	71.3
3	18.44	78.1
4	15.4	58.8
5	15.81	60.5
6	18.6	66.3
7	15.25	56.1
8	15.41	51.9
9	15.26	54.1
10	15.95	65.8
11	20.03	68.2
12	25.11	56.5
13	13.45	56.6

Figure -1 :Before Supercalendering

75 Gloss vs. Pig nt Ratio

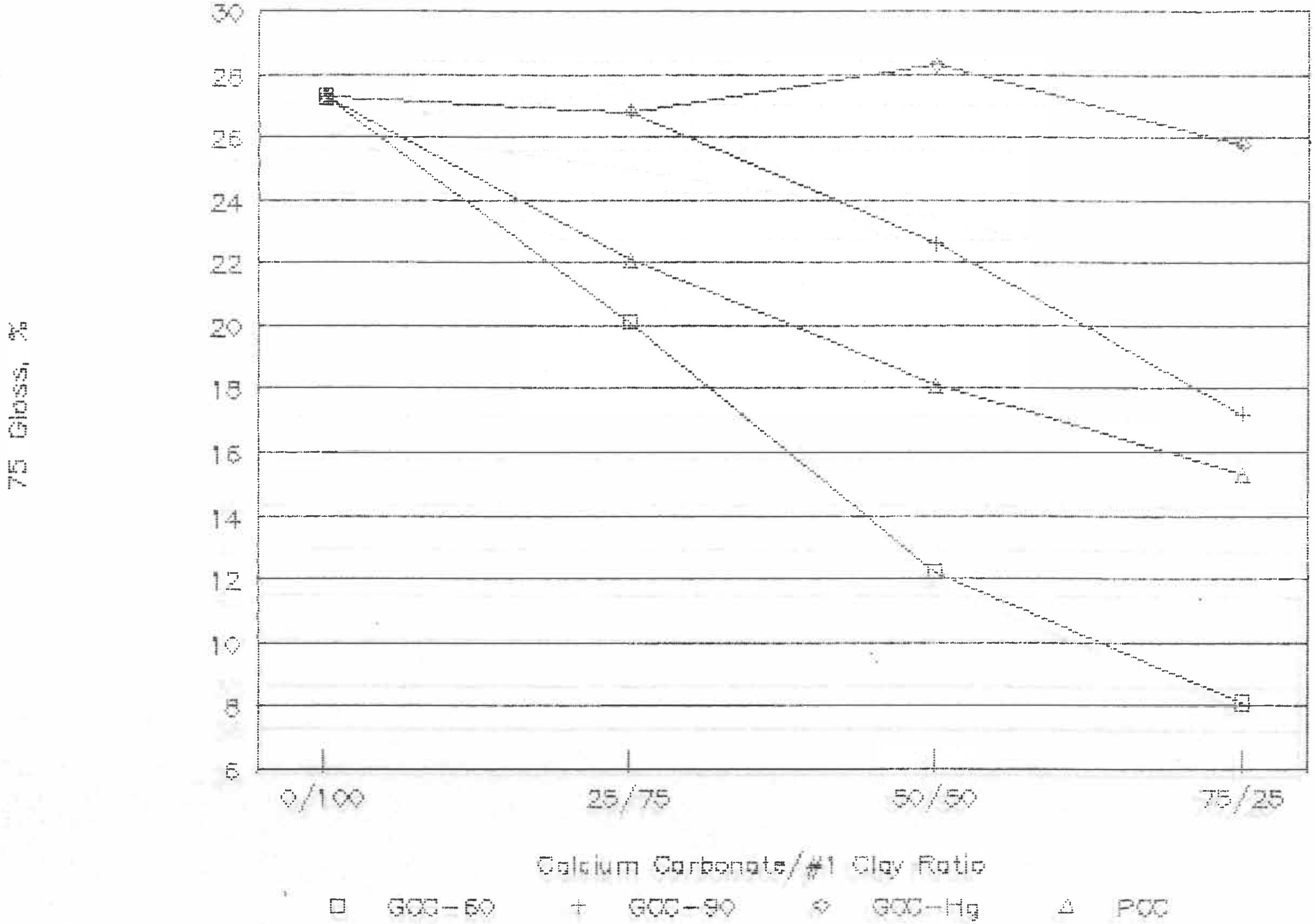


Figure — 2 :After Supercalendering

75 Gloss vs. Pigment Ratio

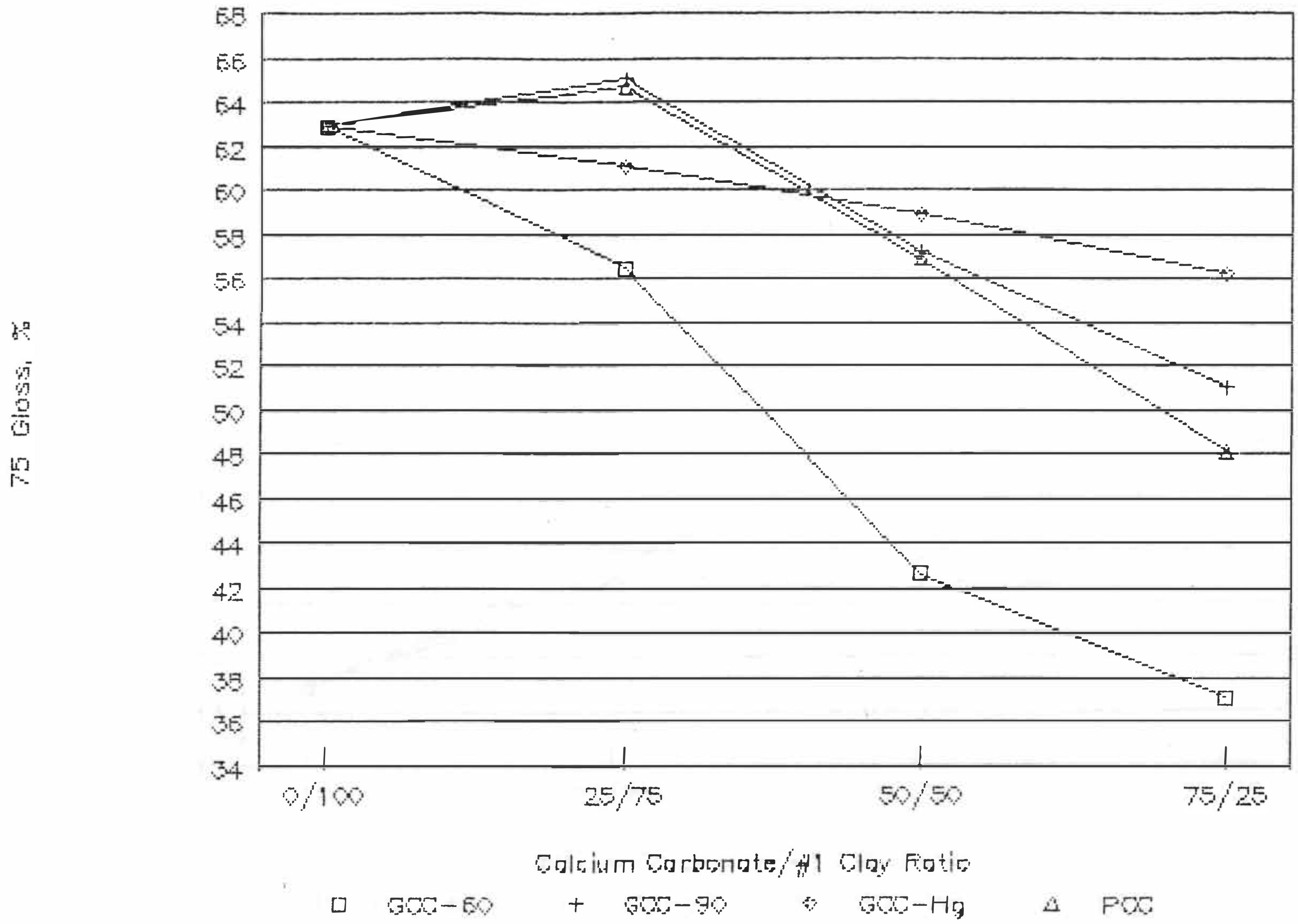
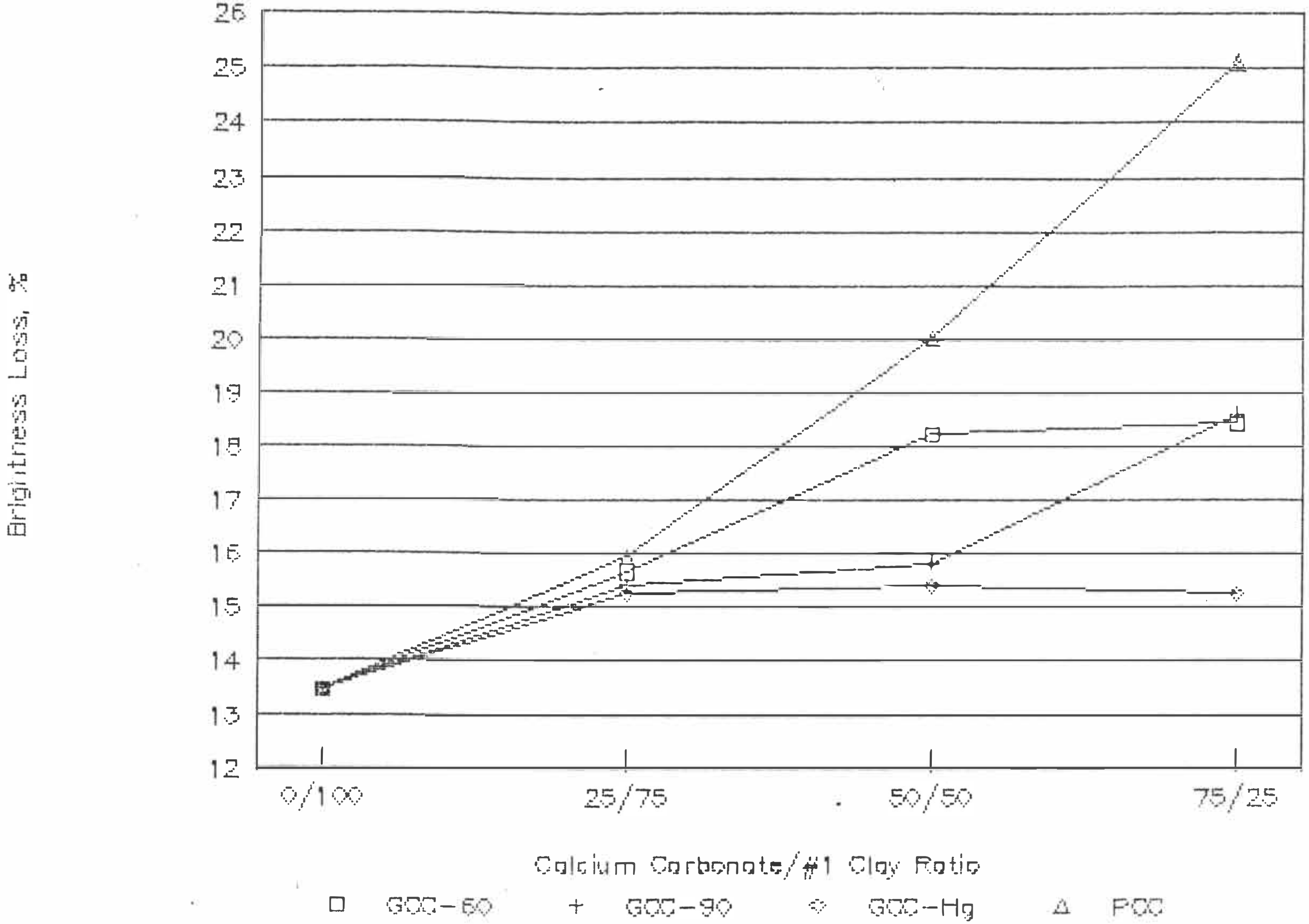


Figure – 3 :After Supercalendering

Brightness Loss vs. Pigment Ratio



DISCUSSION

The calcium carbonate/clay ratio changed from 0% carbonate/100% clay to 75% carbonate/25% clay in increments of 25. The target coat weight was held constant for all runs at 12 +/- 1 gram/m2. Coating color solids were intended to stay constant at 62%, but due to runnability problems some coating solids were decreased; when it was impossible to achieve the target coat weight. The coating color solids are presented in Table III. As the calcium carbonate level increased the solids subsequently increased, but gloss levels in general declined. It appeared the gloss reducing effect of $CaCO_3$ overwhelmed the expected higher gloss that higher solids should have yielded.

When the solids level of a coating is changed, the binder in the coating behaves differently. There is less binder migration into the substrate at higher solids which gives better gloss. The migration of the binder into the substrate reduces the mobility of the pigment particles and effects their ability to reorientate.

Were it possible to keep the solids at 62% for all the coatings a greater reduction in gloss would have been seen. Adding $CaCO_3$ to coatings in increasing amounts improved rheology, high and low shear viscosities, and allowed high solids to be run which somewhat offset the effects on gloss.

There was no significant difference in gloss values if the values in question were within two standard deviations of each other.

Pigment Ratio vs. Gloss before Supercalendering

The GCC-60 which had the largest average particle size decreased gloss most dramatically (See figure 1). The decrease in gloss with increasing amounts of the GCC-60 was caused because the large rhombahedral carbonate particles did not allow tight packing with the clay platelets. This was due to the difference in the particle sizes and shapes of clay and calcium carbonate. The rhombahedral $CaCO_3$ particles were between the clay particles disrupting the "smooth" surface, that should be formed by clay platelets when they are oriented parallel to the paper surface. Therefore, the microtexture of the surface became rougher as the number of carbonate particles increased, and gloss decreased as the amount of $CaCO_3$ increased.

Figure 1 shows that the substitution of GCC-90 did not produce a significant difference in gloss when compared to the 100% clay coating, until the 75% substitution level. The small particle size did not disrupt the surface structure of the coating at lower substitution levels, but at 75% $CaCO_3$/25% Clay there was a decrease in gloss. The decrease resulted because at this substitution level there were not enough clay platelets available to produce a comparable surface smoothness.

The increasing substitution of GCC-Hg, which has the finest average particle size, did not produce a significant difference in gloss when compared to the 100% clay coating(See Figure 1). The particle size and shape of this $CaCO_3$ (90%<1 um, equivalent spherical diameter) did not disrupt the surface structure of the coating significantly with increasing substitution. The small size allowed them to pack tightly with the clay platelets at low levels of CaCO3 addition, and at higher levels the pigment particles were able to pack well together. Since there was no significant change in gloss as clay was decreased and CaCO3 increased, there was not a significant degree of variation in the surface textures.

The substitution of PCC in the coating color did not produce a significant change in gloss until the coating contains 50% CaCO3/50% Clay (See Figure 1). At this level a decrease in gloss occured. The decrease in gloss was caused because the PCC has a very narrow particle size distribution. There were not enough fines to pack between the pigment particles which resulted in greater surface roughness.

Pigment Ratio vs. Gloss after Supercalendering

Supercalendering increased the gloss on the average of 62.1%. This resulted from the realignment of the pigment particles caused by rupture of pigment/adhesive, and/or adhesive/adhesive bonds. The pigment particles were pressed or packed together and the latex polymer was squeezed. This squeezing resulted in the flow of polymer sideways to fill out adjacent depressions. As a result, the microroughness was reduced. The supercalendering action can never remove all the microscopic surface irregularities so there was a limit to its effect on gloss.

The GCC-60 followed the same trend, before and after supercalendering, a decrease in gloss with increasing substitution of GCC-60 (See Figure 2). However, the GCC-60 did yield the greatest percent increases in gloss after supercalendering. Supercalendering also increased gloss of higher CaCO3 levels more than at lower CaCO3 levels. This resulted because coatings with large size particles were more loosely constructed and more easily rearranged when calendered. During calendering the clay particles were realigned and the latex fills in some of the crevices, but there were not enough "small" particles to fill in the gaps produced by the large particles.

The GCC-90's gloss increased more at higher levels of CaCO3 with calendering. The clay platelets were somewhat oriented by the coating application process, therefore calendering had more of an effect on packing the CaCO3 particles, and at higher substitution levels of GCC-90 there were more small particles present to pack together.

The GCC-90 coatings did not produce a significant changes in gloss from the 100% clay coating, until the 75% CaCO3 substitution level (See figure 2). A decrease in gloss at 75% carbonate/25% clay occured, because there were fewer number of clay particles aligned parallel to the paper surface.

The coatings containing GCC-Hg had the lowest increases in gloss after calendering. The smaller the pigment particle size the less the impact calendering had on gloss. The coatings containing GCC-Hg showed the same trend before and after calendering. There was no significant change in gloss when comparing coatings containing GCC-Hg and 100% clay (See figure 2). This resulted because the GCC-Hg has such a small particle size.

The substitution of PCC in the coating color did not significantly effect gloss values until the 75% $CaCO_3$/25% clay coating (See figure 2). At this substitution level the gloss decreased in comparison to the 100% clay coating. This decrease was due to the fewer number of clay platelets in the coating and the narrow particle size distribution of the PCC. Because of the narrow particle size distribution, there were not enough fine particles to fill in the crevices created by the larger particles at the surface.

Pigment Ratio vs. K&N Ink Absorption

The K&N Ink Absorption is measured by the brightness loss of the coating. The more ink absorption the greater the brightness loss. The ink is absorbed into the voids and crevices present on the coating surface. Therefore, much of the rational used in explaining the gloss data was applicable to the brightness losses.

The GCC-60 produced a significant brightness loss with the 50/50 coating color (See figure 3). The higher absorption of ink at this level was the result of voids and pores in the coating. These voids were caused because there were not enough "small" particles in the coating to fill in the crevices and gaps produced by the pigment particles.

The GCC-90 did not produce a significant loss of brightness until the 75% $CaCO_3$ substitution level (See figure 3). This was the same trend as gloss, and occured because of the same reasoning. There were less clay particles available to align and more voids fill.

The GCC-Hg had no significant brightness loss (See figure 3). The surface of the coating was tightly packed and the spaces between clay platelets were filled, because of the small particle size of the GCC-Hg.

The PCC coatings had the most dramatic brightness loss (See figure 3). This was the result of the narrow particle size distribution of the PCC. There were fewer fine particles to fill in the voids created by the larger particles. The voids were more frequent but substantially smaller then those created by the GCC-60.

CONCLUSIONS

1) Calcium carbonate decreases gloss.

2) The coarser the ground calcium carbonate the greater the decrease in gloss.

3) The narrow particle size distribution of PCC was detrimental to gloss and ink absorbtion.

4) The higher solids of the calcium carbonate coatings helped diminish the adverse effect on gloss, but can't make up for it.

5) The coarsest calcium carbonate gave greatest gains in gloss after calendering.

RECOMMENDATIONS

Upon further investigation, I believe it would be useful to determine the pigment volume concentration for each coating, so that a correlation could be drawn between it, gloss, and particle size of the pigment. The image analyzer could also be used to look at the coated surface and observe the pigment particles and their orientation.

Another study could be conducted, in which the coated paper could be calendered to an equal sheet gloss value, as well as an equal number of nips. Correlations could be made to see which $CaCO_3$ gained gloss easiest during calendering, and the effects of calendering on porosity, surface smoothness, ink absorption, opacity, and brightness could be investigated.

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