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# An Evaluation of Ultra-Fine Ground Calcium Carbonates and a Precipitated Calcium Carbonate for Properties in Coated Paper

Gordon A. Erickson Western Michigan University

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Erickson, Gordon A., "An Evaluation of Ultra-Fine Ground Calcium Carbonates and a Precipitated Calcium Carbonate for Properties in Coated Paper" (1979). Paper Engineering Senior Theses. 134. [https://scholarworks.wmich.edu/engineer-senior-theses/134](https://scholarworks.wmich.edu/engineer-senior-theses/134?utm_source=scholarworks.wmich.edu%2Fengineer-senior-theses%2F134&utm_medium=PDF&utm_campaign=PDFCoverPages)

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#### AN EVALUATION OF ULTRA-FINE GROUND CALCIUM CARBONATES AND A PRECIPITATED CALCIUM CARBONATE FOR PROPERTIES IN COATED PAPER

**by** 

Gordon A. Erickson

#### A Thesis Submitted in partial fulfillment of the course requirements for the Bachelor of Science Degree

Western Michigan University Kalamazoo, Michigan April 1979

#### Abstract

This thesis is a study of four ultra-fine ground calcium carbonates and one precipitated calcium carbonate. These five carbonates were evaluated at five levels of carbonate in a coating formulation based on the weight of pigment. The evaluation of the performance of the five carbonates is concluded from brightness; opacity, Brookfield viscosity, K & N Index, gloss, and gloss development. As the level of carbonate increased, so did the brightness of the coated sheet for all of the carbonates. All carbonates at all five levels of addition show the same relevant opacity. Differences in viscosity for the carbonates are essentially due to different particle size, shape, and distribution. Three of the carbonates showed a relative linear increase in the K & N Index **with** increased levels of carbonate addition, while the other two carbonates went through a minimum K & N Index value. One of the carbonates was an outstanding exception when comparing gloss, but showed increased gloss with increased levels cf carbonate addition. Further studies into the areas of viscosity, ink absorption, and gloss for coated papers containing calcium carbonate are indicative for understanding the effects of these calcium carbonates.

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#### Introduction

The paper industry is one of the largest users of pigments and fillers in the United States. The paper industry's consumption of pigments and fillers is estimated to be over 2.5 million tons annually.

Total consumption of calcium carbonate in 1976 was estimated to be 217 million pounds, of which 77% was for precipitated carbonate and the remaining 23% was for the natural ground carbonates. The 167 million pounds of precipitated carbonates comprises *over* 50% of the precipitated carbonate used in U.S. industry. This year (1978) the expected usage of calcium carbonate is 242 million pounds, an 11% increase from 1976 levels. The use of natural ground calcium carbonate is expected to increase from 23% to 26% of the total carbonates used annually (1).

The supply of ground natural carbonate is adequate to meet expected levels of demand. The demand for natural carbonate pigments and fillers will continue to grow. This growth is partially due to natural carbonates replacing or extending the short supply of precipitated carbonates. Suppliers of natural carbonates foresee an increase in the market share for the natural carbonates where better costeffectiveness can be achieved with precipitated carbonates. This potential market has led to companies producing one or more grades of ultra-fine calcium carbonates.

#### Product Description

Calcium carbonate can be classified by two categories: the natural products made directly by physically grinding limestone, and the precipitated products made by chemically reacting various raw materials. The two categories are further broken down into several groups based on particle shape and size. The natural products have a larger particle size and a larger range of particle size. The precipitated products have more nominal variations in particle size and specific• particle shape giving mere apparent differences in performance properties. Chemical purity is higher for the precipitated products than the natural products. The major difference is in the contained impurities as found in the magnesium and silica analyses  $(2)$ .

Calcium carbonate occurs in nature as either of two crystalline polymorphs: calcite or aragonite. Calcite falls into hexagonal-scalenohedral crystal class in hexagonal system (3). In nature its commonly observed habits or crystal structures are in prismatic, tabular, carboid, rhombohedral, and scalenohedral form. Precipitated calcite is usually found in the rhombohedral or scalenohedral crystal structures.

Aragonite falls into the dipyramidal crystal class in the orthorhombic system. The crystal structures are elongated prismatic or acicular form. Aragonite is less common

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in nature than calcite due to its metastability. Commercial grades of precipitated aragonite are characterized by crystals having parallel sides and large length-to-width ratio (Figure 1). Aragonite precipitation is favored by the presence of divalent or sulfate ions (3).

Commercial precipitated calcium carbonates are usually exclusively one form or the other. Mississippi Lime has a product M-60 which is of the calcite crystal structure. Pfizer produces Albagloss which is aragonite crystal structure (2).

Typical chemical analyses are shown in Table 1. Table 2 shows various properties of calcium carbonates. While there is very little difference .in pH, a high pH indicates free lime and a high surface potential (3). As seen in Table 2, the coarser natural products had the lowest oil absorption. Low absorption values are found with low surface area values. The ultra-fine ground limestone has a larger surface area value than most precipitated carbonates, but a lower oil absorption value. This is explained by agglomerations or "clustering" provided by interparticle capillaries which promote an absorptive action not found with discrete particles as in ground limestone (2).

The amount of siliceous material present in carbonates is a measure of abrasiveness of the pigment. The Valley Abrasion values in Table 2 show the fine ground limestone to be quite abrasive, but the ultra-fine ground limestone

was found to be no more abrasive than the precipitated carbonates. This demonstrates that particle size of carbonates does control the abrasiveness.

Ground limestone has been used in paper coatings to give the paper a dull or low-gloss finish. With the development of the ultra-fine ground limestone, these carbonates have found a place in paper coatings where gloss development is important. Ultra-fine grades of ground limestone, finer than 0.1 mm, are difficult to handle and have a tendency to be transparent (3). While ultra-fine ground limestone can have as good gloss development, a few coarse particles can improve gloss; therefore, a narrow range of particle size is needed.

For carbonates both natural and precipitated to be used in coatings, they have to be well dispersed. The natural carbonates have been found to disperse easily and to be agglomerate-free. The precipitated carbonates have been more difficult to disperse and have the tendency to have agglomerates. The precipitated products need high solids content and high shear to disperse well. It has been generally accepted that the polyphosphates such as Calgon T or TSPP were the most effective dispersants. Now dispersants such as Dispex N-40 are recommended.

Table 3 shows viscosity of precipitated carbonates at various solids content. Figure 2 shows the rheograms of those carbonates.

Calciwn carbonates are seldom used as the sole pigment

*in* a coating fonnulation. They have made up between 5% and 50% of the coating formulations and up to 70% for the ultrafine ground limestone to obtain properties comparable with conventional coating formulations. Calcium carbonates contribute to brightness, opacity, smoothness, and ink receptivity to coated paper as well as to gloss development. To get these desired properties, it is necessary to define the carbonates with respect to size, shape, and chemical components. For the fine particle size obtained from the precipitated products or the ultra-fine ground limestone, the particle size, shape, and chemical potential are all related and affect the flow characteristics of the coating color (Tables 4 and 5). Tables 6 and 7 (2) show how sheet properties vary with different coating formulations.

Tappi methods will be used to analyze the carbonate contribution to the coated paper as well as some more accepted printing analyses for paper. The coated paper will be tested for brightness, opacity, gloss, gloss development, and K & N ink. The coating formulation will be tested for viscosity using Brookfield Viscosity.

#### Experimental Procedure

This thesis is concerned with the physical properties of coated paper. The physical properties to be tested for are brightness, gloss, opacity, and K & N Index.

Brightness is important for the aesthetic value. The precipitated products usually have q brightness level of 1 to 2 points higher than the natural products. This difference is mainly due to impurities of the carbonates. A GE-Brightness meter is to be used.

Gloss also has aesthetic value. The gloss on coated paper as well as gloss development with 2, 4, and 6 nips on the laboratory calender stack at 1500 pli will be evaluated using Tappi methods.

The opacity evaluation will entail Tappi Opacity (contrast ratio) C<sub>0.89</sub>, which is equal to  $R_0/R_{0.89}$ . Here,  $R_0$ and R<sub>0.89</sub> are the reflectance of values obtained when the papers are backed by a black cavity and by a surface having an absolute reflectance of 89%, respectively. Opacity is important for the reason of show-through. Show-through of printing ink is a detriment.

Five different formulations will be used for each sample. These are 90 parts of clay to 10 parts of carbonate; 80 parts of clay to 20 parts of carbonate; 70 parts of clay to 30 parts of carbonate; 60 parts of clay to **40** parts of carbonate; and 50 parts of clay to 50 parts of carbonate.

The clay to be used will be a #1 coating clay, Hydrasperse, manufactured by Huber Clays. Both the clay and the carbonates will be made up ahead of time at 70% solids. The dispersant to be used is Dispex N-40 at an addition level of 0.1% for the clay and 0.5% for the carbonates. The binders to be used are Dow Latex-620 and Stayco M at 10% and 5%, respectively.

The different formulations will be made up at the time of use to avoid changes with time. The colors will be tested for Brookfield Viscosity before running the color on the Kegan Coater at Western Michigan University's Paper Science and Engineering Department. The paper used is a raw base stock from Consolidated Papers. The coated paper samples will be stored in a constant humidity- and temperaturecontrolled room for later evaluation. The samples will be tested for brightness, gloss, gloss development, opacity, and K & N Index.

#### Discussion of Results

#### Brightness

All of the carbonates show an increase in brightness **with** increased concentration of carbonate, as seen in Figure 3. Brightness contribution from the carbonates is a function of impurities in the carbonates as well as the particle size and size distribution of the carbonates.

As expected, as shown in Figure 3, D exhibited the lowest brightness at all levels of addition. This is due to its particle size and particle distribution of an upper limit of 10 microns and 90% less than 6 microns and 50% less than 2 microns. The other ultra-fine ground carbonates have an upper-limit size of 5 microns and a distribution of 90% less than 2 microns and 50% less than 0.8 microns in size. PCC has a limit of 10 microns and a distribution of 90% less than 3 microns and 50% less than 1.1 microns.

While PCC has a particle size and distribution greater than A, B, and C, the increased level of brightness can be accounted for in the chemical analysis of magnesium and silica (2).

#### Opacity

No significant changes in opacity were observed, as seen in Figure 1, with any of the samples or level of addition of carbonate. Opacity is a function of the Refractive index.

All of the carbonates used have a Refractive index of 1.66. While the Refractive index for the sample is the same, the differences in opacity can be explained by the different particle size distribution. Hagemeyer stated that the most effective particle size is 0.2-0.35 microns (3).

#### Viscosity

A, PCC, and C were used in the predispersed slurry form. B and D were dispersed using Dispex N-40 at 0.5% based on pigment weight. All slurries were at 70% solids.

The differences in viscosity, as shown in Figure 4, are essentially due to different particle size, shape, and distribution. The dispersant(s) may be a contributing factor, also. Relationships between the physical descriptions are not fully understood and have yet to be reduced to theory.

#### K & N Index

K & N Index is the ratio of brightness difference before and after ink exposure and is expressed as a percentage. As noted in the literature review, low oil absorption values are due to low surface area. Ultra-fine ground carbonates have higher surface areas, higher than the precipitated carbonates, but lower oil absorption values. These higher absorption values are from the precipitated carbonate forming interparticle capillaries, promoting absorption. These capillaries are not able to form from discrete particles, but from a "clustering effect" (2).

Effective particle packing produces a less porous coating structure which limits the absorption of the ink. Higher effective particle packing is obtained from natural ground carbonates than from precipitated carbonates, yielding lower K & N Index values than for the precipitated carbonates. This is due to the lesser extent of uniform particles in the ultra-fine ground carbonates. No specific theory has been developed to predict K **&** N Index values in coating colors **with** clay on calcium carbonate.

As seen in Figure 5, an ultra-fine ground carbonate, B, does have equivalent K **&** N Index values as the precipitated carbonate, PCC; � also shows the same linear increase in values, but at a lower level, as the addition level of carbonate increases.

C and D both show values that are explained by the effective particle packing. These two ultra-fine ground carbonates gave lower K & N Index values until approximately 30% addition of carbonate. This follows in increased effectiveness of particle packing with increased addition of carbonate giving a less porous structure. After the 30% addition level, an increase *in* K **&** N Index demonstrates increasing ink absorption. These increased values are explained by decreasing effective particle packing and/or that the "clustering" effect is now dominant.

#### Gloss and Gloss Development

Gloss and gloss development are primarily a function of particle size of the pigment and the "steps" that the pigment takes with increased pli (4). Shape factors do not influence gloss to any great extent. R. W. Hagemeyer demonstrated that the needle-shaped calcium carbonates and the rhombic calcium carbonates produce similar packing tendencies when used with clay. The minimum packing was obtained at an 80% clay/20% carbonate formulation. With increased levels of carbonate, the packing increases (5).

All of the carbonates followed a linear relationship of gloss and gloss development. With the exception of one carbonate, A, all carbonates showed decreased gloss with increased levels of carbonate, as seen in Figures 6-9. All carbonates follow Dennison's "steps," yielding increased gloss with increased pli as expected.

Increasing the level of addition of carbonate beyond the 80:20 ratio increasing the packing of the pigment particle allows for more "steps" to be obtained. With A being the exception, all other carbonates gave decreased gloss with increased levels of carbonate. This is expected; the level of decrease in gloss is directly related to the particle size and size distribution of the carbonates.

Hagemeyer (3) stated: "While the particle size and particle shape of the calcium carbonate are important, it should be recognized that the particle size and particle

shape of other pigments in the mix will also have a pronounced influence on the coating properties" (p. 63). The calcium carbonate A yields results that can be explained by packing tendencies providing for increased "steps" with increased level of carbonate. The deviation from the other three ultra-fine ground carbonates and the precipitated carbonate is because an ideal mix was obtained with A, clay, adhesives, and dispersants.

#### Conclusions

The brightness of the coated paper is a function of the brightness of the pigments used. Carbonate having a higher brightness than of the clay caused the brightness to increase with increased levels of carbonate. PCC showed the highest brightness at all levels of addition, while D showed the lowest brightness. Only 5 points of brightness difference occurred over the total range of carbonates looked at.

The opacity did not change significantly with increasing levels of carbonate in the formulations. A total range of 1.3 points was obtained with the five carbonates at five levels of addition. PCC did show the highest opacity.

Brookfield Viscosity does differ significantly between the carbonates used. A and PCC did show increased viscosity with increased levels of addition. A had the highest viscosity, while both had a maximum viscosity between the 30-40% addition levels.

B, D, and C all showed decreasing viscosities with increased levels of carbonate. B had the lowest viscosity.

K & N Index did show significant differences between the carbonates. B, A, and PCC all showed relative linear increases of K & N Index with increased levels of carbonate. D and C showed a decreasing Index with increased levels of carbonate up to approximately 30% after which the Index increased with further additions of carbonate.

Gloss and gloss development for all of the carbonates, except for A, showed the same relative pattern, that gloss decreases with increased levels of carbonate at the same level of calendering. A gave an increase in gloss with increased levels of carbonate (Figures 6-9).

Gloss development for a specific level of carbonate (Figures 10-11) showed the same relative pattern of gloss development as did the specific carbonate at increasing levels of calendering (Figures 12-13). The increase in gloss tended to level out for all five carbonates as the number of nips at 1500 pli increased.

#### Recommendations

Carbonates are becoming more widely used in coating formulation. Rheology of coating colors needs to be understood to be able to predict their effect on the coated surface structure.

Smoothness of a coated sheet is a requirement for good printability. Ink absorption is also a desirable property of a coated sheet. The effects of carbonates, physically and chemically, need further study to help understand the reason for increased ink absorption.

What makes up an ideal mix to give the desired end results of increased gloss with increased levels of carbonate is a question many persons in the field of coatings would like to have answered.

### Literature Cited

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- 3. Hagemeyer, R. W., Tappi Monograph 38, p. 39.
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### **APPENDIX A**

Literature Data



# Chemical Analysis of Calcium Carbonate





# Various Properties of Calcium Carbonate Pigments





Viscosities of a Precipitated Calcium Carbonate Dispersed at Varying Solid Levels

**Table 3** 

N 0



Table 4

a<sub>80</sub> parts No. 1, high brightness clay

20 parts calcium carbonate pigment

12 parts SBR latex

4 parts ethylated starch







Note: Viscosity measured at "as coated" solids level at 62%.

a60 parts No. 1, high brightness **clay** 

40 parts calcium carbonate pigment

12 parts **SBR latex** 

4 parts ethylate starch

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Sheet Properties for Coating Formulation No. 1



# Sheet Properties for Coating Formulation No. II



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### **APPENDIX B**

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# Experimental Data



Viscosity (cP)

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	A		B		$\mathsf{C}$		D		<b>PCC</b>	
Ratio	M	SD	M	<b>SD</b>	M	<b>SD</b>	M	<b>SD</b>	M	SD
90:10	29.76	2.567	27.31	0.999		27.36 2.114			29.02	1.784
80:20		28.32 2.393	28.75	1.197		28.59 1.914	32.11	0.828	29.35	2.688
70:30	29.16	2.276	29.70	2.065		26.20 1.618	32.11	0.828	29.54	3.181
60:40	29.42	3.039	28.56 2.154			28.43 2.542	31.25	1.897	31.20	2.211
50:50	28.28	2.107	27.65	0.765	24.12	3.217	29.49	0.306	27.52	1.838

Coat Weight  $(g/m^2)$ 

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# Brightness

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Ratio	$\mathbf{A}$		$\mathbf{B}$		$\mathbf C$		D		<b>PCC</b>	
	M	SD	M	<b>SD</b>	M	SD	M	SD	M	SD
90:10	94.06	.3354	94.37	.3990	94.32	.1920	94.28	.6182	94.35	.6642
80:20	93.83	.1750	94.16	.5540	94.00	.6440	94.42	.3300	94.78	.5115
70:30	94.06	.0890	93.98	.4260	93.66	.2700	94.28	.3457	94.72	.4294
60:40	93.71	.6280	93.70	.4200	94.31	.3132	94.19	.3210	94.53	.3640
50:50	93.98	.2160	94.21	.4060	93.48	.5260	93.90	.5240	94.52	.2301

Opacity

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	$\mathbf{A}$		B		C		D		<b>PCC</b>	
Ratio	M	<b>SD</b>	M	<b>SD</b>	M	SD	M	<b>SD</b>	M	SD
90:10	22.26	1.767	32.34	2.078	25.75	3.128	23.90	3.672	30.64	3.750
80:20	22.46	4.172	32.16	2,644	24.81	2.940	22.36	2.708	35.89	3.070
70:30	28.28	2.616	36.24	3.596	18.89	1.780	21.30	1.826	35.48	4.944
60:40	30.96	2.388	39.28	3.116	23.97	3.964	25.70	1.986	25.92	4.944
50:50	31.38	2.004	37.33	1.222	28.74	4.318	26.28	3.283	39.12	3.509

K & N Index



 $\mathbf{1}$ 

**Gloss Development: 0 Nips** 

Ratio	A		B		C		D		<b>PCC</b>	
	M	<b>SD</b>	M	SD	M	SD	M	SD.	M	SD
90:10				69.36 3.356 57.21 3.065 56.78 1.842			62.25	2.895		62.65 3.024
80:20	60.45 1.253		60.76 2.297		55.97 2.280		56.93	1.792		51.44 3.123
70:30	64.90 2.638		60.18 1.570			51.91 1.150	51.27	1.959		59.26 2.829
60:40	67.96	1.881		57.89 2.476	$52.51$ $1.408$		45.14	2.405		52.05 2.985
50:50			64.60 2.446 55.13 0.479			47.73 1.962	38.10	2/357		54.93 1.504

**Gloss Development: 2 Nips** 

	A		B		C		D		<b>PCC</b>	
Ratio	M	<b>SD</b>	M	SD	M	SD.	M	SD	M	SD
90:10	78.53	2,4420	68.80	1.8660		67.78 0.6854	73.80	1.8220 70.82 1.2400		
80:20	75.10	2.5220		68.38 1.8200		64.47 2.2200	67.58	1.1230 68.30		2.9500
70:30	73.22	0.9538		67.09 2.4850		62.38 1.3430	61.57	1.1750 67.57		2.0240
60:40	77.52	1.2630	66.88	0.9393		61.83 1.5080		56.98 1.8240 63.18		1.8810
50:50	73.82	2.9760	62.37	$0.1668$ 57.61 1.6180			48.20	1.9110	65.94	1.8620

Gloss Development: 4 Nips

*w w* 

Ratio		A		B		C		D		<b>PCC</b>	
	M	SD	M	SD	M	<b>SD</b>	M	<b>SD</b>	M	<b>SD</b>	
90:10	83.20	1.4580		72.89 1.5960 72.02 1.0840				78.36 1.6700	75.90	0.8697	
80:20	83.86	2.8060	72.90	1.1640		68.83 1.7060	72.27	1,2200	71.38	2.8480	
70:30	82.44	1.0510	72.93	$0.5095$ 66.95 1.8140			69.00	1.9600	71.56	1.2760	
60:40	84.83	1.8360		68.90 1.5730		67.12 1.3900		60.73 1.8450	67.78	1.1820	
50:50	79.00	2.2630	67.00	1.0210		61.02 2.2230		55.54 1.7800 69.64 1.2120			

**Gloss Development: 6 Nips** 

*w �* 



### Points Decrease in Brightness--Calendering

### **APPENDIX C**

 $\label{eq:2.1} \frac{1}{4\pi}\int_{0}^{\infty}\frac{d\mu}{\mu}\left(\frac{d\mu}{\mu}\right)^{\mu}d\mu.$ 

Graphic Analyses





Figure 2. Rate of shear versus torque.















![](_page_49_Figure_0.jpeg)

Points gloss (80:20) versus<br>number of nips. Figure 10.

![](_page_50_Figure_0.jpeg)

Points gloss (60:40) versus<br>number of nips. Figure 11.

![](_page_51_Figure_0.jpeg)

Points gloss (B) versus number<br>of nips. Figure 12.

![](_page_52_Figure_0.jpeg)

Points gloss (C) versus number<br>of nips. Figure 13.