Calcium Carbonate Particle Size Effects on Titanium Dioxide Light Scattering in Coatings

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TITLE: Calcium Carbonate Particle Size Effects on
                                Titanium Dioxide Light Scattering in Coatings

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ABSTRACT

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Coatings

Jason Wai Pan Boke

Titanium dioxide (TiO_2) is an essential component in a white paint formulation due to its excellent light scattering ability. TiO_2 also happens to make up most of the raw materials cost. Viable replacements to TiO_2 do not currently exist in a feasible manner. Rising costs in the recent TiO_2 supply shortage have forced coatings formulators to find a balance between cost and performance. One method includes partial substitution of TiO_2 with cheaper material such as calcium carbonate ($CaCO_3$), which serves to occupy volume.

The purpose of this study was to compare the coating spread rate of paints with varying TiO_2 and $CaCO_3$ pigment volume concentration (PVC). Different sized $CaCO_3$ particles were used in this study. A series of PVC ladder studies were performed at keeping $CaCO_3$ PVC constant. Paints were formulated at the same volume solids to minimize variability. Weighed coating draw-downs were prepared to measure the contrast ratio. The coating spread rates were obtained with the DuPont Spread Rate program, which relies on Kubelka-Munk relationships, which takes into account the physical properties of the paint. These spread rate values were compared to one another across type and size to find common trends. Critical pigment volume concentration (CPVC) values were determined through regression of the spread rate values and compared to oil absorption tests.

It was found that replacement of up to 20 PVC of TiO_2 with $CaCO_3$ could marginally increase the spread rate, thus increasing the efficiency of TiO_2. The spread rate increased modestly as similarly sized extender particles were initially introduced, then dropped at higher extender levels. Data analysis revealed that CPVC was influenced based on the size and amount of the extender particle present, which can be used to predict resin demand of a paint system.

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1. Introduction

1.1 Titanium Dioxide Price Trends

Titanium dioxide (TiO_2) follows an uneven market cycle with short periods of a supply crunch and longer periods of oversupply. Factors include procurement of ore, plant operation, as well as financial and economic effects. Regardless of the factors, the price of TiO_2 is relatively stable with the exception of the supply crunch periods. Shown in Figure 1 is the historical and forecast price of TiO_2 from 1990 to 2015 (Fasano & Adamson, 2012).
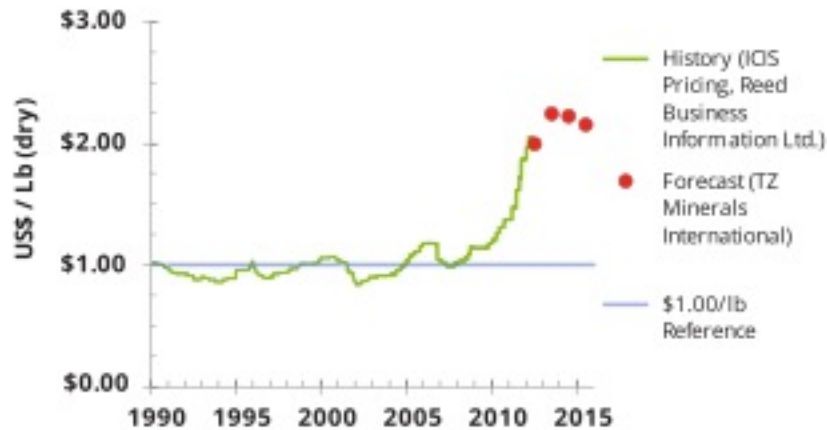
Figure 1: North America historical average and forecast price of TiO_2 (Fasano, 2010)

The latest TiO_2 supply shortage started in 2010 where the average price increased from $1 to over $2 per pound (Fasano & Adamson, 2012). The price hike is especially significant because TiO_2 makes up anywhere from a third to a half of the raw material costs (Cardinal, Francis, & Scriven, 2009). Due to market competition, the price increase is not completely passed onto the end consumer (Cardinal et al., 2009). As a result, paint formulators have been forced to reevaluate their paint systems in a manner to reduce

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costs without compromised paint properties. One common method involves partial substitution or replacement of TiO_2 with a cheaper mineral. It is however important to mention that material costs are not limited to TiO_2 as there are other ingredients common in paint.

1.2 Early Paints

The earliest known use of paints dates back more than 30,000 years to cave paintings in Spain (Brock, Groteklaes, & Mischke, 2010). These paints were simply mixtures of colored earth, soot, grease, and other natural substances. The ancient Greeks, Romans, and Egyptians used natural resins and raw materials to decorate and identify statues, tools, vessels, and buildings (Brock et al., 2010; Goldschmidt & Streitberger, 2007). These natural ingredients include vegetable gums, starches, and amber. In China and India, shellac resins and beeswax were used over 2000 years ago as a decorative coating which also doubled as a protective function (Gennadios, Hanna, & Kurth, 1997). The earliest paint formulation dates back roughly 900 years to a German goldsmith and monk, Rodgerus von Helmershausen (Brock et al., 2010; Goldschmidt & Streitberger, 2007). His formulation described the manufacturing of paint by mixing linseed oil and amber, referred to as paint boiling, which was further refined and developed into the Industrial Revolution (Brock et al., 2010; Goldschmidt & Streitberger, 2007). The demand for paints dramatically increased into the Industrial Revolution. As the amount of iron used for making goods and buildings increased, the concern for rust quickly followed. Additionally, as sea-trade increased, the demand for marine coatings followed. The earliest paint factories appeared as early as 1790 in England and quickly spread to Holland and Germany (Brock et al., 2010).

It is important to note that the most of the raw materials in paints and coatings made into the early 1900s were of natural origins. Synthetic materials were not yet introduced aside from a few pigments. Downfalls to paints at this time include extended drying time due to the use of the oil-based paints. This time also marked the start of the first continuous production line by Henry Ford as cars were being mass-produced. The result was a move to spray coating of a quick drying nitrocellulose based paint with solvent contents as high as 80% (Brock et al., 2010; Goldschmidt & Streitberger, 2007). Synthetic polymer chemistry also developed at this time with Carothers and others in the 1920s (Painter & Coleman, 2000). Numerous resin systems were developed in succession from one another from the 1930s to 1940s. Included are vinyls, ureas, alkyds, acrylics, polyurethanes, melamines, and epoxy based resins. Changes to paint technology in the past 40 years have focused on reducing solvent content in paint formulations. This is due to increased regulation of volatile organic compounds (VOCs) in paint formulation. Primary developments in paint technology today include further reduction of VOCs for environmental benefits and optimizing paint formulations for specific functions.

1.3 Components of a Pigmented Paint

Paints and coatings are typically synonymous in colloquial speech. The accepted definition of a coating is a product based on organic binders, which provides a cohesive, non-absorbent, protective film (Brock et al., 2010). Differences in the composition of the various coatings systems are presented in Table 1. Common to all three coating systems are the resin and additive. Clear coats are optically inactive; therefore pigments and fillers are not present. Powder coatings are not in a liquid medium; therefore a solvent is not present. Paints are liquid materials that are optically opaque coatings that form when

applied by brushing, rolling or spraying (Brock et al., 2010; Goldschmidt & Streitberger, 2007). In other words, paints are a type of coating that cover up a background, but it is important to note that not all coatings are paints. Paints are composed of ingredients that can be put into one of four categories: film formers, pigments and fillers, additives, and solvents. Factors that are considered in a paint formulation include its ability to flow, mechanical properties, as well as appearance when prepared, during, and post application of the coating.

Table 1: Typical Composition of Various Coating Systems

		Coating Type		
		Pigmented Paint	Powder Coating	Clear Coat
Material Category	Resin	Yes	Yes	Yes
	Additive	Yes	Yes	Yes
	Solvent	Yes	No	Yes
	Pigment & Extender	Yes	Yes	No

1.3.1 Film Formers

Resins are the precursors to binders, which result in film formation in a paint system. In this context, resins, binders, and film formers can be though of as the same material category. The technical definition of a binder is the non-volatile part of a paint excluding the pigments and filler, which includes the non-volatile additives (Brock et al., 2010). These film formers contain macromolecule-forming substances, or polymers as well as oligomers. Examples include acrylics, alkyds, amino resins, cellulose derivatives, epoxies, polyesters, urethanes, polyvinyl acetates, and polyvinyl chlorides. The purpose

of the film former is to provide a cohesive coating on a substrate, holding together the other non-volatile components. These film-formers are typically categorized into natural or synthetic substances.

Natural substances for use as film formers include natural resins and oils. Colophony is a natural resin extracted from pine trees as balsam and fractionally distilled, isolating abietic acid (Brock et al., 2010). The presence of a conjugated double bond and carboxyl group is an important chemical feature. Colophony is rarely used as is due to poor natural resistance to yellowing, water resistance, and compatibility. Natural oils or fatty oils were important film forming agents which were able to convert a low viscosity liquid into a solid (Goldschmidt & Streitberger, 2007). These naturally occurring oils are triglycerides, triesters of glycerol and fatty acids. The drying and hardening process is the result of autoxidation and crosslinks.

Some of these natural substances have been chemically modified to optimize their coating properties. Cellulose derived compounds are an example of natural substances that are modified for use as film formers. Cellulose is widely present in plants, but cannot be used directly due to poor solubility in water. Modification of the hydroxyl groups enables solubility in water to act as a film former. Use of natural rubber as a film former is possible after chemical modification due to brittleness resulting from oxidation and insolubility in coating solvents (Brock et al., 2010).

Table 2: Differences between step-growth and chain-growth polymerization

Step-growth Polymerization	Chain-growth Polymerization
Slow polymerization rate	Fast polymerization rate
Rapid loss of monomer early in the reaction	Some monomer remains even at long reaction times
Similar steps repeated throughout reaction process	Three distinct reactions
Molecular weight increases slowly initially	Molecular weight increases rapidly initially
Bonds formed by functional groups	Carbon-carbon bonds
No initiator needed	Initiator needed

Synthetic resins came about in the 1920s with the advancements in polymer chemistry. The primary benefits of synthetic resins are that products can be tailored with specific properties with nearly unlimited availability. The different resin systems are mentioned above, all of which are either step-growth or chain-growth polymerization (Wicks, Jones, Pappas, & Wicks, 2007). Chain-growth reactions typically have three reactions – initiation, propagation, and termination. Step-growth polymerizations are reactions between bifunctional or multifunctional monomers without an initiation or termination step. Key differences between step-growth and chain growth polymerization are presented in Table 2.

Polymers dispersions are created through emulsion polymerization. Polymer dispersions are transparent white liquids low in viscosity. This system contains spherical polymer particles generally referred to as latex particles. Emulsion polymerization involves addition of slightly soluble monomers and water-soluble initiators in an aqueous media.

1.3.2 Pigments & Fillers

Pigments are particles that are used for their ability to impart color in a coating material. Characteristics common in pigments include extreme optical characteristics, particles smaller than 10 μm, being insoluble in water and most organic solvents, and being chemically inert or chemically stable (J. H. Braun, 1993). Pigments and dyes are both colorants – the difference being that pigments are insoluble whereas dyes are soluble in the application medium. Fillers are also particles that are insoluble in a paint system, but are purposed to increase volume in a paint system. Fillers are also commonly referred to as extenders and function as inert pigments. Fillers are significantly cheaper than pigments and contribute little to no optical properties.

Table 3: Comparison between inorganic and organic pigments

Property	Inorganic Pigment	Organic Pigment
Particle Size	Larger	Smaller
Scattering Power	Higher	Lower
Color Intensity	Lower	Higher
Surface Characteristic	Hydrophilic	Hydrophobic
Heat Resistance	Higher	Lower

Pigments can be categorized as being white, black, colored inorganic, and colored organic. Additionally, there are specialty functional pigments for corrosion protection. The most important white pigment is titanium dioxide (TiO_2), which will be discussed in further detail in Chapter 2. Other white pigments are considered less important as their optical performance is inferior. Black pigments include carbon black. Colored pigments operate by absorbing and scattering light at different intensities at different wavelengths. Colored inorganic pigments are typically variants of iron oxides (Goldschmidt & Streitberger, 2007). Use of colored organic pigments has grown due to the presence of

heavy metals in their inorganic counterparts. Organic pigments have much more distinct colors with a higher color purity. A comparison between the organic and inorganic pigments is presented in Table 3 (Brock et al., 2010). Organic pigments are usually azo based, polycyclic based, or metal-complex based. Benefits of the inorganic pigments include stability and chemical resistance.

Fillers can come from a variety of materials, in different shapes and sizes. Shapes vary from blocks to rods and can be smooth or porous. Their sizes can vary anywhere from nanometers to microns depending upon the application and requirements in the paint system. The majority of filler materials are natural in origin, which helps to reduce cost. Fillers can also be used to improve tensile strength and/or control the degree of gloss of coatings. Common filler materials include carbonates, silicon dioxide, silicic acids, silicates, and sulfates (Brock et al., 2010; Goldschmidt & Streitberger, 2007; Wicks et al., 2007).

These pigments and extenders are commercially available in solid or slurry form. Slurry is an aqueous solution that contains dispersed pigments or extenders. In a paint application, the pigment and extenders are eventually dispersed in some sort of medium. The dispersion process involves 3 steps – wetting, separation, and stabilization (Wicks et al., 2007). It is important that particles are separated because aggregation and flocculation of these particles result in diminished optical properties due to the decrease surface area exposure.

1.3.3 Additives

An additive is a substance added to a coating material in small quantities in order to impart specific properties to the coating material. Additives can be thought of as an alternative to hasten the film forming system and/or pigment system in most cases for compatibility. Additives are divided into various groups, catering to a specific function. A few specific examples include defoaming agents, wetting and dispersing agents, surfactants, flatting agents, rheology modifiers, corrosion inhibitors, light stabilizers, and biocides. Some additives serve multiple functions and can influence multiple properties.

1.3.4 Solvent

Solvents are liquids that comprise one or more components that are volatile under specified drying conditions that dissolve film-forming agents without chemical reaction. Additionally, the solvent lowers the viscosity of a paint formulation for easier application. The term solvent can also be thought of as a vehicle used to apply a coating material, as there is a movement to reduce VOCs in current paint formulations. Most coatings, including waterborne coatings still contain some volatile solvents.

2. Titanium Dioxide

World production of titanium dioxide (TiO_2) is over 4 million tons per year, most of which is used in coatings applications (Brock et al., 2010). As mentioned earlier, TiO_2 is used as white pigment in paint application. To date, a better white pigment has not been discovered as a replacement or alternative to TiO_2. Production of TiO_2 pigments started in the 1920s and rose dramatically in the 1930s replacing lithopone, zinc oxide, and lead containing compounds as some examples. The Chloride Process was introduced in the 1950s, producing pure rutile TiO_2. Production of TiO_2 in aqueous dispersions started in the 1970s for better incorporation into waterborne coatings. Current trends in TiO_2 technology have involved surface treatment to minimize crowding effects for better efficiency.

2.1 Physical Properties

Table 4: Physical Property Differences Between TiO_2 crystal structures

Property	Anatase	Brookite	Rutile
Crystal System	tetragonal	tetragonal	tetragonal
Point Symmetry	D_{4h}	D_{2h}	D_{4h}
Refractive Index	2.5	2.6	2.7
Density (g/cm^3)	3.8-3.9	3.9-4.1	4.2-4.3
Mohs' hardness	5.5-6.0	5.5-6.0	6.5-7.0
Melting Point (˚C)	915*	750*	1830

*=rearrangment to rutile

There are three main crystal structures associated with TiO_2 – anatase, brookite, and rutile. Brookite is rare and unstable. Differences between the three crystal structures affect various physical properties, some of which are summarized in Table 4. Rutile TiO_2 is commonly used in coatings application due to improved optical properties. Anatase TiO_2 use includes paper pulp due to lower hardness for processing. Brookite TiO_2 is rare

in nature and typically rearranges to the rutile crystal structure (Davis, 1982). This

naturally occurring oxide of titanium is mined and processed to make TiO_2 particles.

$$H_2O + O_2 \xrightarrow{hv/TiO_2} \bullet OH + HO_2 \bullet$$
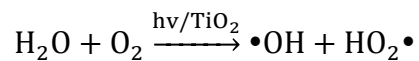
Figure 2: Photocatalytic Reaction on TiO_2 surface

It is important to note that TiO_2 particles are surface treated, usually with alumina

and/or silica. TiO_2 can generate radicals in the presence of UV light, shown in Figure 2,

which can degrade the paint or coating (J. Braun, Baidins, & Marganski, 1992). The

surface serves as a barrier to prevent the generation of these radicals. As a result,

commercially available TiO_2 particles are typically not pure. Surface treatment can

account for as much as 20% of a TiO_2 product.

2.2 Production Methods

There are two methods for producing titanium dioxide pigments – the Sulfate

Process and the Chloride Process. The Sulfate Process dates back to the early 1900s and

is the older process that employs aqueous chemistry, whereas the chloride process is the

newer process, commercialized by DuPont in the 1950s (J. Braun et al., 1992; Hanna,

2009). Following the different manufacturing processes, the TiO_2 particles undergo

finishing steps, depending on their desired quality.

2.2.1 Sulfate Process

The sulfate process can produce anatase and rutile titanium dioxide.

Manufacturing steps include digestion, clarification, hydrolysis, and calcination (J. Braun

et al., 1992; Hanna, 2009). Ore is used as a starting material that must be broken down.

Clarification is the process of removing impurities. Hydrolysis involves the use of water

to break apart bonds in a chemical reaction. Calcination is a thermal treatment of a material, hydrous titanium dioxide in this case, to create titanium dioxide. Key reactions are depicted in Figure 3. Titanium bearing ore such as ilmenite ($FeTiO_3$) is dissolved in sulfuric acid. The iron sulfates are removed and remaining solution dissolved in water. The remaining solution is heated and precipitated as hydrous titanium dioxide and grown to proper particle size and surface treated as necessary (J. Braun et al., 1992; Davis, 1982; Hanna, 2009). Rutile pigments are produced with rutile seed crystals added during the hydrolysis step (J. Braun et al., 1992).

$$FeTiO_3 + 2\,H_2SO_4 \rightarrow FeSO_4 + TiO \bullet SO_4 + 2H_2O + H_2$$

$$TiO \bullet SO_4 + 2H_2O \rightarrow TiO_2 \bullet H_2O + H_2SO_4$$

$$TiO_2 \bullet H_2O \xrightarrow{\text{heat}} TiO_2 + H_2O$$
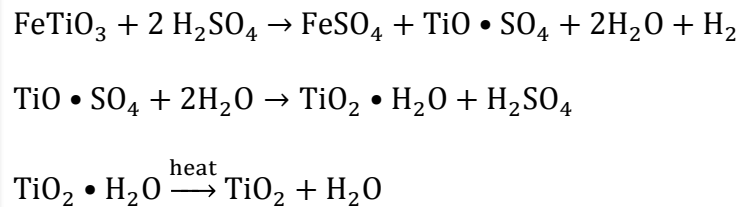
Figure 3: Key Reactions to the Sulfate Process

2.2.2 Chloride Process

$$3\,TiO_2(\text{ore}) + 4\,C + 6\,Cl_2 \rightarrow 3\,TiCl_4(\text{gas}) + 2\,CO_2 + 2\,CO$$

$$TiCl_4(\text{gas}) \rightarrow TiCl_4(\text{liquid})$$

$$TiCl_4(\text{gas}) + O_2 \rightarrow TiO_2(\text{solid}) + 2\,Cl_2$$
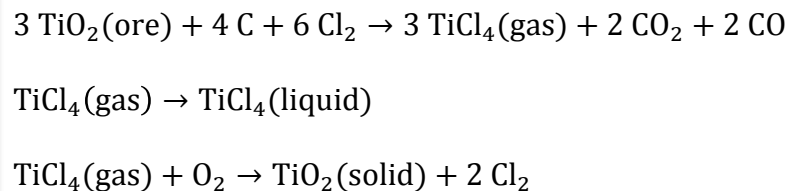
Figure 4: Key Reactions to the Chloride Process

The chloride process offers waste disposal, energy, and quality advantages over the sulfate process (J. Braun et al., 1992). Examples include production of rutile pigments having narrow particle size distributions. Additionally, there is material efficiency as chlorine can be recycled in the reaction. Key manufacturing processes in the chloride process includes chlorination, purification, and oxidation. Key reactions to the chloride

process are presented in Figure 4. Titanium ore is heated up with chlorine gas and coke to produce titanium tetrachloride, or 'tickle', and other metal chlorides, which are then fractionally distilled, which is purified, converting the gas to a liquid (J. Braun et al., 1992; Davis, 1982; Hanna, 2009). The purified titanium tetrachloride is then vaporized and reacted with air to form TiO_2 and chlorine.

2.2.3 Finishing Steps

Table 5: Classification of dry TiO_2 pigments according to ASTM D476

	Type I	Type II	Type III	Type IV	Type V	Type VI	Type VII
Crystal structure	anatase	rutile	rutile	rutile	rutile	rutile	rutile
Typical application	white exterior house paint and interior uses	low-medium percent PVC	high percent PVC	exterior coatings requiring high durability	exterior coatings requiring high durability with high gloss	medium-high percent PVC	low-high percent PVC
Min. TiO_2 content, %	94	92	80	80	90	90	92
Min. moisture content when packed, %	0.7	0.7	1.5	1.5	1	0.7	0.7
Specific gravity	3.8-4.0	4.0-4.3	3.6-4.3	3.6-4.3	3.6-4.3	3.6-4.3	4.0-4.3

Production of TiO_2 particles doesn't stop at the chloride and sulfate process. There are more than 400 different types of TiO_2 pigments commercially available (Brock et al., 2010). ASTM D476 describes and classifies seven types of dry TiO_2 products, taking composition, end application, and performance properties into account, which is presented in Table 5.

As mentioned previously, TiO_2 particles are typically not sold as pure compounds due to their surface treatments. TiO_2 particles are coated in water by precipitation or adsorption techniques onto the surface, with silica and alumina being the most common

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inorganic oxides used. These oxides come in a variety of sizes and shapes, which cater

the TiO_2 particle to specific applications, such as altering surface roughness, which

affects gloss. Additional finishing steps may include further grinding to prevent

aggregation of particles for optimal TiO_2 performance. If prepared as slurry, additives are

used to ensure a dispersed and stable medium for the TiO_2 particles.

2.3 Mechanism in Paint

Pigments are effective due to their unique optical properties. In the case of white

pigments, the 'whiteness' is due to the scattering of light by the pigment. The light

scattering is the mechanism that contributes to hiding and can be explained from optical

theories. White pigments are unique in that the appearance of white is due only to

scattering, whereas colored pigments may also rely on selective scattering as well as

absorption of light.

Table 6: Refractive Index (R.I.) of Common Materials in Paint

Pigments	R.I.	Media	R.I.
Silica*	1.49	Vacuum	1.00
Calcium Carbonate	1.63	Air*	1.00
Clay	1.65	Water	1.33
Lithopone	1.84	Polyvinyl acetate resin	1.47
Zinc oxide	2.02	Vinyl resin	1.48
Zinc sulfide	2.37	Acrylic resin	1.49
TiO_2 (rutile)	2.73	Styrene butadiene resin	1.53

* = approximate

The refractive index can be described as the degree of bending of light as it passes

through a material. This value is a dimensionless value and is typically referenced to light

traveling in a vacuum. Larger refractive indexes reflect a greater degree of bending of

light. The refractive index of pigments and film formers are presented in Table 6. In the

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case of paint, the interface is between that of the pigment and binder material, not air –

except when formulating at high volume solids. As a result, the actual refractive index

difference is lower as typical film formers have a refractive index around 1.5, which is

similar to that of extender materials. It is unsurprising that the high refractive index of

TiO_2 is desired in paint, as there are currently no practical alternatives commercially

available.

2.4 Benefits in Paint

In addition to contributing to hiding power through its optical properties, TiO_2 is

also used in paint for UV absorption and anti-microbial properties. These intrinsic

properties are additional reasons why TiO_2 has not been replaced.

2.4.1 UV Absorber

UV absorption is one mode of action as a light stabilizer. Other modes include

radical interceptors, quenching agents, and hyrdoperoxide decomposers (Brock et al.,

2010). Most polymers, including paints, are susceptible to degradation due to UV light.

UV light is also damaging to biological systems. The degradation is due to the generation

of propagating radicals. Rutile TiO_2 absorbs more UV light than anatase TiO_2, as shown

in Figure 5 (DuPont, 2007). Recall that the absorbance is inversely related to the

reflectance, which is localized scattering. It is also important to note that the optimum

particle size for UV light absorbance varies over different wavelengths (Wicks et al.,

2007). Despite being a UV absorber, as mentioned earlier, TiO_2 is also prone to generate

radicals when reacted with UV light and water leading to a process called chalking. The

overall photocatalytic reaction is presented in Figure 2. Chalking is the process of the

degradation of the binder and exposure of the pigment that is no longer bound. Again, the

surface treatment of TiO_2 particles is performed to decrease the photoactivity, slowing

down the reaction.
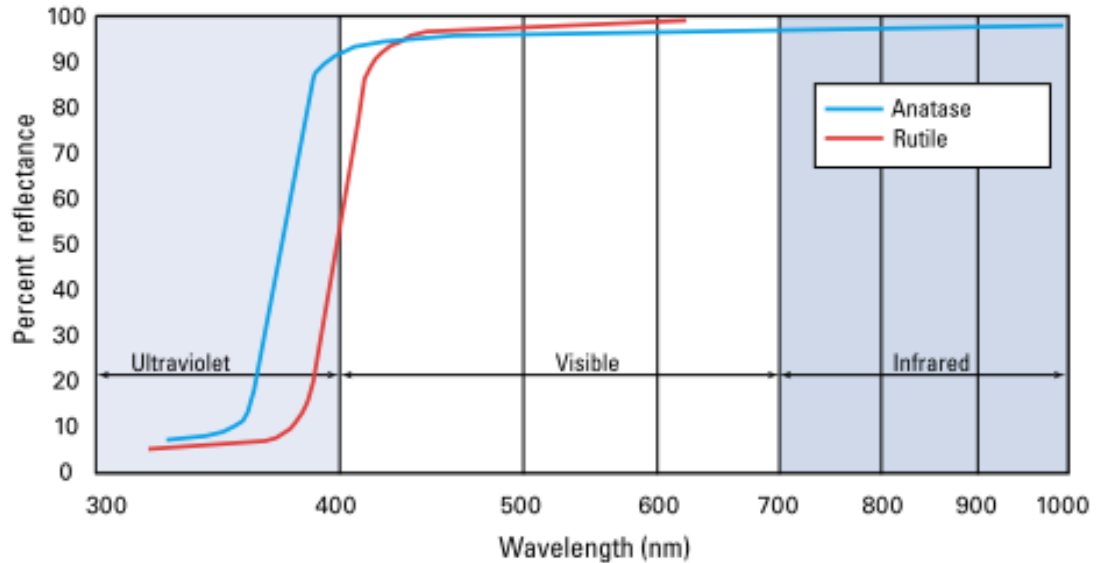
Figure 5: Reflectance of TiO_2 Pigment at Various Wavelengths (DuPont, 2007)

2.4.2 Antimicrobial Properties

Biocides are needed in coating formulations to control bacteria growth for a

variety of reasons, which affect paint application and durability. Reasons include smell

and pressure due to gas generation, degradation of the cellulose derivatives in paint, as

well as blotchy discoloration on applied paint. TiO_2 is not used as a biocide, but has some

antimicrobial properties due to the photocatalytic reaction mentioned earlier (Chung, Lin,

Tsou, Shi, & He, 2008; Xing et al., 2012).

3. Calcium Carbonate

Filler or extender particles such as calcium carbonate ($CaCO_3$) primary serve as replacement for the binder material. Reasons include the lower cost of filler materials or formulation above critical pigment volume concentration (Section 4.3).

Table 7: Physical Properties of Calcium Carbonate

Property	$CaCO_3$ (calcite)
Refractive Index	1.63
Density (g/cm^3)	2.7
Mohs' hardness	3
Melting Point (°C)	1339

The primary difference between pigments and fillers are the difference in cost. Fillers can also be thought of poorly functioning pigments. It is unsurprising that fillers are poorly optically active. The physical properties of $CaCO_3$ are presented in Table 7. $CaCO_3$ is an example of a filler material and it is unsurprising that the refractive index of $CaCO_3$ is significantly lower than TiO_2 (RI = 2.73). Some naturally available forms of $CaCO_3$ include chalk, calcite, and aragonite (Brock et al., 2010). Chalk and calcite are used as filler material. Chalk is a natural $CaCO_3$ up to 1 μm in diameter from the shells and skeletons of small organisms (Brock et al., 2010). Calcite is a natural $CaCO_3$ derived from limestone and is generally 2-3 μm in diameter, commonly used in paint formulations (Brock et al., 2010). Smaller particles (as small as 0.6 μm) are also possible in synthetic form as precipitated calcium carbonate.

4. Packing and Scattering Theory

The refractive index is one way of expressing light scattering performance. In the case of TiO_2, a number of factors, including particle size, particle size distribution, shape, and dispersion affect the scattering power (E. Thiele & French, 1998). Additionally, aggregation and flocculation alter the scatter performance.

4.1 Mie Theory
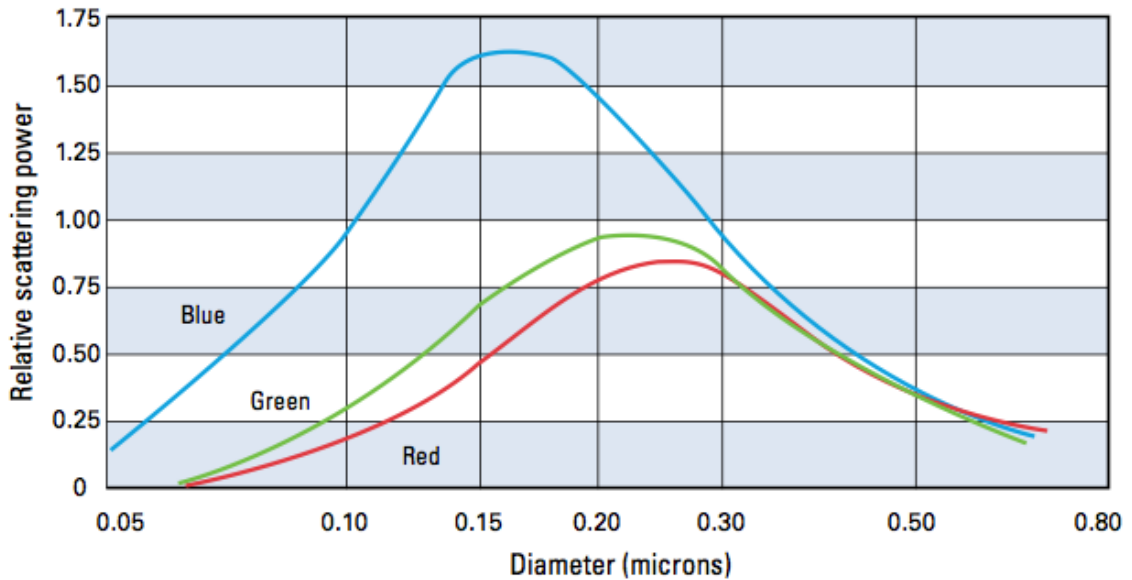
Figure 6: Relative Scattering Power of TiO$_2$ (DuPont, 2007)

The basic foundation to which the scattering ability of TiO_2 is understood is based upon Mie theory. Mie first published a paper in 1908 as a first outline, computing light scattering using Maxwell's electromagnetic theory (Hergert & Wriedt, 2012). Mie theory estimates a general and quantitative model of scattering and absorption of an electromagnetic wave based on a model of one particle that is perfectly spherical. Further refinements have been made to this model to include anisotropic spheres as well as coated spheres (Hergert & Wriedt, 2012). Shown in Figure 6 is the relative scattering

power relationship to size at three colors. The optimum size at which TiO_2 particles scatter light is around 0.2-0.3 μm depending on its wavelength. It is unsurprising that TiO_2 pigments are produced at this size order.
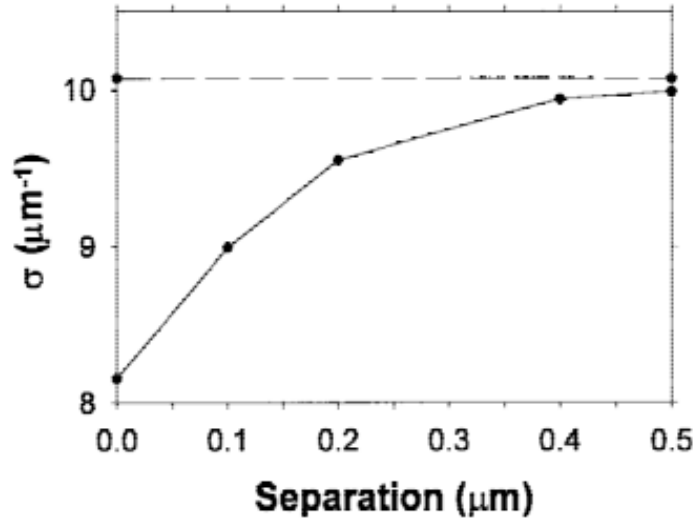
Figure 7: Model of Scattering Loss of Rutile TiO_2 (E. S. Thiele & French, 1998)

On a macroscopic scale, white paint contains more than one TiO_2 particle, which renders limitations to Mie theory. In a paint system, TiO_2 particles are in abundance with a phenomenon called crowding which reduces the scattering ability per particle. The loss of scattering is explained by overlap of optical cross-sections (J. Braun et al., 1992; Winkler, 2003). As TiO_2 particles pack closer together, the available exposed surface area decreases, which lowers scattering efficiency per particle. The crowding effect is well established and has been modeled. Shown in Figure 7 is a model of the scattering power relationship to particle separation distance. There is up to a 20% loss in scattering power as a result of the crowding effects. In essence the flocs of TiO_2 particles can be thought of as one larger particle, which results in dramatically decreased scattering. Much of the

work presented here has a central theme revovled around reducing the crowding effects of TiO_2.

4.2 Kubelka-Munk Theory
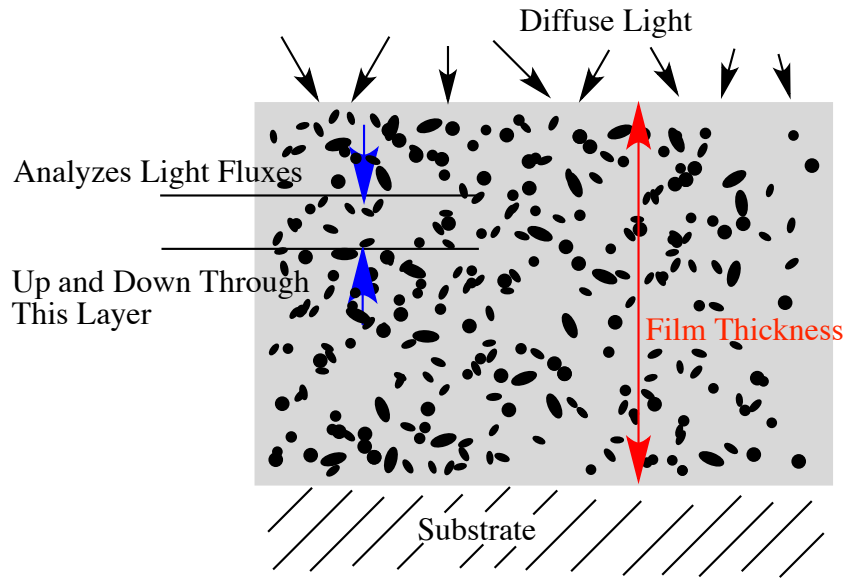
Figure 8: Kubelka-Munk Model

Kubelka-Munk theory is a macroscopic approach to light scattering, where as Mie theory is a microscopic approach. Kubelka and Munk published a set of equations relating contrast ratio, brightness, and quantity of light-scattering material in pigmented film (DuPont, 2002). Kubelka-Munk theory considers the absorption and scattering of light by thin films based on their reflectivites. Shown in Figure 8 is a physical model of Kubelka-Munk theory. The physical model of the theory considers a thin slice of a film and the light passing through it. Kubelka-Munk theory is only descriptive and makes no assumptions concerning the mechanistic reasons for light absorption or light scattering (Winkler, 2003).

$$R = \frac{\frac{(R_g - R_\infty)}{R_\infty} - R_\infty \left(R_g - \frac{1}{R_\infty}\right) e^{SX\left(\frac{1}{R_\infty} - R_\infty\right)}}{(R_g - R_\infty) - \left(R_g - \frac{1}{R_\infty}\right) e^{SX\left(\frac{1}{R_\infty} - R_\infty\right)}}$$

Figure 9: Kubelka-Munk Equations

The Kubelka-Munk equation is shown in Figure 9. The Kubelka-Munk equation

expresses the reflectance, R, by considering the background (typically black) reflectance,

R_g, the scattering power, SX, and the reflectance of a thick film, R_∞, such that the

reflectance does not change. The SX term itself is dimensionless but is a product of the

scattering coefficient, S, and the amount of scattering material or thickness, X. The S

term is constant for each coating formulation. Altering the amount of coating changes the

SX value. The X term can be expressed in units of film thickness or coverage area,

making the units of S the reciprocal of X (e.g. mil^{-1} or ft^2/gal). The X term can also be

referred to as the spread rate.

Kubelka-Munk relationships can be graphically represented with opacity charts

by interrelating reflectances over a black and white substrate, R_∞, and SX. These

Kubelka-Munk relationships were first plotted by hand in the late 1930s (Biermann,

1995). Computers can now generate these Kubelka-Munk relationships for more precise

calculations. An example of an opacity chart is presented in Figure 10. The reflectances

over a black and white substrate can be measured to give corresponding SX and R_∞

values from the opacity chart. The R_∞ associated for each formulation is considered

constant and does not change. The SX values can be interpolated at various contrast

ratios, increasing as the contrast ratio increases due to a larger quantity (X) used. Since

the scattering coefficient is constant, the X value can be estimated at different contrast
ratios.
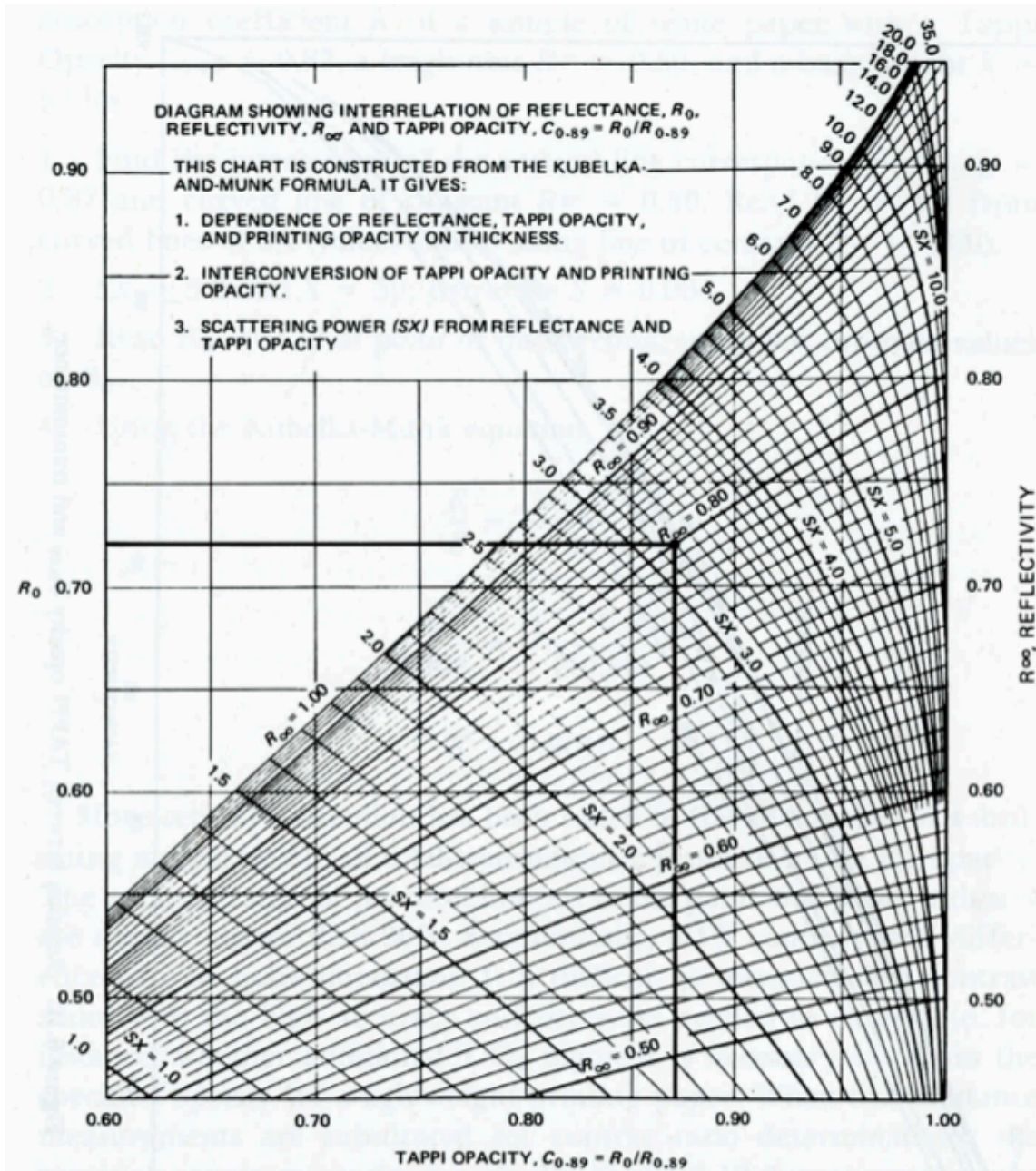
Figure 10: Kubelka-Munk Opacity Chart (Hunter & Harold, 1987)

4.2.1 Contrast Ratio

The purpose of a white paint is to cover or hide the underlying substrate. This can be measured subjectively by 'eyeballing' how well the paint 'hides'. The hiding power of paint can also be described in a quantitative manner through its contrast ratio. The contrast ratio is the measurement of the hiding of paint without distinction between contributions from light scattering and absorption (J. H. Braun, 1993). The contrast ratio is expressed as the quotient of reflectance of a film (paint) measured over a black and white substrate, performed on an opacity drawdown chart. This value can be expressed as a whole number or as a decimal with a maximum value of 100 or 1. The reflectance value is defined as the Y tristimulus value. Complete hiding is a common term that refers to a contrast ratio of 0.98 or greater.

4.3 Pigment Volume Concentration
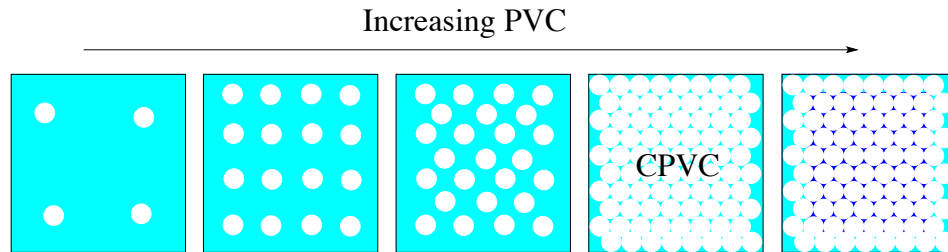
Increasing PVC

Figure 11: Model of System with Increasing PVC

Pigment volume concentration (PVC) is the most widely accepted quantitative description of paint film composition (J. H. Braun, 1993). PVC is expressed as volume percentage of the pigments and fillers to that of the volume of the dry film expressed as a whole number. Volume is used rather than weight because pigments scatter based on

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volume. PVC values are quantifiable between 0 – 100, but these values do not necessarily carry over to other pigment-resin systems.

Shown in Figure 11 is a 2D simple model of a coating with increasing PVC. This simple model assumes uniform sized TiO_2 spherical particles (white spheres) surrounded by the binder material (teal). At low PVC, TiO_2 particles scatter light at near their maximum ability. As additional TiO_2 is added to the system, binder is replaced by the TiO_2 particles. A consequence of the replacement of binder with TiO_2 particles is that the TiO_2 interparticle distance begins to decrease, lowering scattering efficiency. The scattering efficiency continues to decrease until the particles are essentially touching each other, at which point it reaches the critical pigment volume concentration (CPVC). CPVC is defined qualitatively as the point at which there is just enough binder material to fully envelop the pigment particles. Above CPVC, there is insufficient binder material to envelop the pigment particles, which results in air voids (blue). The TiO_2 particles continue to have decreased scattering efficiency due to crowding effects, but there is a greater refractive index difference between TiO_2/air (2.73 and 1.00) than TiO_2/binder (2.73 and ~1.5), which improves opacity. Above CPVC, these air voids begin to form an interconnecting network. Changes in the film properties are most apparent when compared below and above CPVC. Mechanical and chemical properties deteriorate as PVC increases.
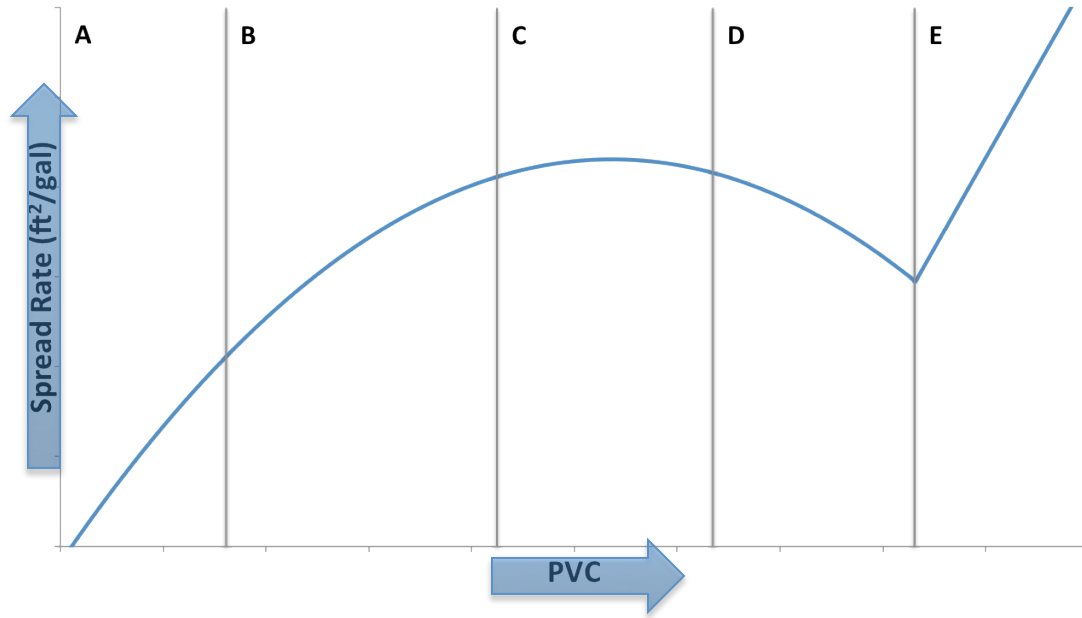
Figure 12: Typical PVC Effect on Spread Rate

Since complete hiding is typically desired in a paint application, the contrast ratio
is not an effective method to quantify paint performance. The spread rate is an alternative
scale that can be used to estimate the paint performance in a quantifiable manner for
application purposes. The units of spread rate are typically ft^2 per gallon. Spread rate
values typically reflect paint films at complete hiding. It is unsurprising that the quantity
of pigment affects the spread rate of paint due to their optical properties. The spread rate
generally increases with PVC, but this generalization is not completely true. A typical
spread rate to PVC relationship with TiO_2 is presented in Figure 12. This figure can be
broken down into 5 parts. As TiO_2 is first incorporated into a paint formulation (region
A), there is maximum scattering effect, which can be observed by comparing the slope.
This simply means that the TiO_2 particles are spaced apart and have maximum scattering.
With additional TiO_2 incorporated (region B), crowding effects become apparent with
decreased scattering efficiency. The spread rate continues to increase, but not to the

degree as in region A. Notice that the slope begins to decrease from region A into region B. The spread rate apexes in region C as addition of TiO_2 has negligible effects on the spread rate. Again, this is due to crowding effects. Further addition of TiO_2 results (region D) in lower spread rate due to crowding of multiple TiO_2, which can be thought of as a larger particle. Regions A-D is the consequence of lower scattering efficiency as the TiO_2 particles pack closer together. Despite having maximum scattering efficiency in region A, the spread rate value is low because the TiO_2 particles are spaced 'far' apart. The result is that additional paint is needed to achieve the desired hiding effect. The CPVC point begins in region E and is characterized with a dramatic increase in the spread rate slope, which often exceeds that of region A. The increase in spread rate is due to the introduction of a secondary network of air voids due to the insufficient binder coverage. Specifically, the spread rate increase is the result of an increased refractive index difference between the pigment and its surrounding medium, specifically pigment-air and binder-air interfaces. Light scattering results from the refractive index difference as well as the number of surface interfaces.

The sample model provided above is an example of a one pigment using the same resin system. In the case of pigment blends, this simple model still applies even in the case that pigment blends contain different particle sizes. Void space will always be present as pigments are packed together. The voids contain either air or binder, or other particles when using pigment blends. The void space of packed pigments depends on the pigment size. Larger particles form larger voids and vice versa. In the case of different sized particles, the smaller sized particles are able to pack themselves in the void spaces.

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Paints can vary in PVC as certain PVC ranges are better fit for different applications. Paints are generally not formulated above CPVC with solely TiO_2. Reasons include the price of TiO_2 pigment and diminished paint properties above CPVC. Additionally, fillers are typically used to reduce the crowding effects of TiO_2. Examples of diminished properties include lower gloss and tensile strength as well as being more porous and higher susceptibility to rusting. The property changes all converge around CPVC (Asbeck, 1992). CPVC values vary dramatically with the primary factors due to pigment type, particle size, and pigment flocculation (Wicks et al., 2007). The general trend is that CPVC increases with increased particle size and wider particle size distribution. Flocculated pigments tend to have low CPVC values due to trapping of solvents with the pigment while in the binder, which will then evaporate, forming air voids (Wicks et al., 2007). There are multiple methods to determine CPVC. In many cases, accuracy and/or precision are poor due to the method of measurement. Additionally, CPVC typically varies depending on the method. Examples of these methods include tinting, measuring film density, or calculation from oil absorption tests.

4.3.1 Oil Absorption

Oil absorption (OA) tests can be performed as a method to calculate CPVC. The OA of a pigment is the grams of linseed oil per 100g of pigment needed to form a paste-like texture. ASTM methods D281 and D1483 both provide similar methods to determine the OA value of a pigment or pigment blend. Both methods use linseed oil and a spatula to incorporate the pigment and linseed oil until a paste is formed. The equation used to relate OA and CPVC is shown in Figure 13. CPVC is expressed as mL of pigment per

100 mL of film, ϱ is the density of the pigment, OA is oil absorption value, and 93.5 is a factor that take into account the density of linseed oil in g/mL per 100 mL of film.

$$CPVC = \frac{1}{1 + \frac{OA * \varrho}{93.5}}$$

Figure 13: Equation Relating OA and CPVC

OA tests and the calculations are useful despite the lack of accuracy and precision in some cases. These OA tests assume that the wetting properties of linseed oil are similar to that of the paint system and that any flocculation that occurs in the OA test is carried over to the paint system (Brock et al., 2010). Additionally, when working with pigment blends, OA and CPVC estimates cannot be accurately made due to packing dynamics that result from different sized particles. The void space of packed pigments depends on the pigment size, assuming they are all the same shape. If smaller materials are able to fit in the voids, the available surface area increases.

5. Materials and Methods

All materials were obtained from commercially available sources. Physical

properties were obtained for the prepared materials by use of a CEM microwave oven to

obtain weight solids for slurries (TiO_2 and $CaCO_3$) and use of an oven, set to 105°C for

72 hours in the case of the masterbatch. A VMA-Getzmann Dispermat was used to blend

and mix the materials. Density was measured in weight per gallon using a 8.3 mL U.S.

(Baltimore) Midget Cup.

5.1 Material Formulations

To simplify and ensure consistency in paint formulation, it was decided

beforehand to keep the volume solids of the individual components for the white paint

formulations equal to one another. The ingredients that made up the white paints came

from a masterbatch and slurries of TiO_2 and $CaCO_3$ in different ratios. The masterbatch

includes the film formers and additives for the paint system. Slurries contain pigments in

a dispersed aqueous form. The pigments were prepared in slurry form, then diluted to the

same volume solids level to that of the masterbatch.

Table 8: Physical Properties of Pigments and Extenders used in this Study

Pigment Material	R-741 Slurry R-931	R-746 Slurry R-706	Omyacarb 15	Omyacarb UF
Median Particle Size (μm)	0.36	0.55	15	0.70
Min TiO_2 by weight (%)	80	93	N/A	N/A
Pigment Density (g/mL)	3.84	4.10	2.70	2.70

A summary of the pigment and extender physical properties used in the PVC

ladder study are presented in Table 8. White paints were made into PVC ladders with

varying concentrations of TiO_2 and $CaCO_3$. A PVC ladder is a study conducted through

formulation of white paints with increasing PVC. R-741 and R-746 (DuPont) slurries of

TiO$_2$ were made into separate PVC ladders and compared to one another. Additional

PVC ladders were made containing R-746 with either Omyacarb 15 or Omyacarb UF

(Omya) slurry in varying concentrations. R-741 and R-746 slurries contain R-931 and R-

706 (DuPont) grades of TiO$_2$ pigment, as appropriate. These TiO$_2$ grades are

differentiated from each other by their surface treatment and median particle size. R-931

pigments contain 80% weight solids of TiO$_2$ with a median particle size of 0.55 μm,

whereas R-706 pigments contain 93% weight solids TiO$_2$ with a median particle size of

0.36 μm. Omyacarb UF contains CaCO$_3$ particles with particle sizes on the order of TiO$_2$

particles (0.70 μm), whereas Omyacarb 15 particles are significantly larger than that of

the TiO$_2$ particles (15 μm).

Table 9: Solids Content of Masterbatch

Masterbatch	TFW-182	TFW-182 with Acrysol RM-8W
Density (lb/gal)	8.63	8.66
Weight Solids (%)	25.48%	24.22%
Density of solids (lb/gal)	8.55	9.75
Volume Solids (%)	23.61%	21.49%

The masterbatch used for this study was an internal formulation from DuPont,

designated as TFW-182 Emulsion Gloss Masterbatch. Additional thickener, Acrysol RM-

8W (Dow), was incorporated into the masterbatch due to initial concerns of pigment

settling, due to the low solids of the masterbatch, especially of concern at high TiO$_2$ PVC

due to the pigment density. The Acrysol RM-8W thickener was initially prepared by 50%

dilution by weight in distilled water. Following preparation 4.4% by weight of the diluted

Acrysol RM-8W thickener solution was added to the masterbatch. The additional

thickener was incorporated into the masterbatch using a VMA-Getzmann Dispermat dropwise with a pipet, and then mixed at 1000 RPM for 10 minutes. TFW-182 utilized an acrylic latex polymer as the binder material in the paint formulation. This masterbatch contained film formers as well as additives for the white paint. This premade masterbatch was used to minimize the variation in the paint components due to the number of paint samples that were to be made. A summary of the solids and density values for the TFW-182 masterbatch is shown in Table 9. The masterbatch with added thickener the material used in making the white paints. The volume solids were found by calculating for the solids density from the bulk density and weight solids.

TiO_2 (R-741 and R-746) was already available in slurry form (72-77% weight solids) and were diluted with distilled water such that the volume solids was equal to that of the masterbatch, which was 21.49% volume solids. The slurry was diluted as each PVC ladder was prepared to avoid settling of the TiO_2 particles. TiO_2 particles would settle out if the TiO_2 slurries were diluted in bulk beforehand, as TiO_2 has a higher density than the water content of the diluted slurry (78.51% volume solids). The dilutions were determined through a series of calculations similar to the masterbatch in finding density and weight solids and converting to a volume basis.

$CaCO_3$ extenders (Omyacarb 15 and Omyacarb UF) were prepared into slurry form. The extender slurry was made in a high-speed Dispermat mixer with a grind at 78% weight solids and letdown to 72% weight solids in distilled water. Added to the Omyacarb slurries was a dispersant, Tamol 1124 (Dow), at 2.2% by volume. The extender slurry was eventually diluted with distilled water such that the volume solids were equal to that of the masterbatch (21.49% volume solids). Dilutions were performed

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as each PVC ladder was made to avoid settling of the extender particles in the slurry due to the absence of thickener in the slurry.

5.2 Paint Preparation

OmyaCarb 15

TiO$_2$	0	5	10	15	20	25	30	35	40
0	x	x	x	x	x	x	x	x	x
5	x	x	x	x	x	x	x	x	x
10	x	x	x	x	x	x	x	x	x
15	x	x	x	x	x	x	x	x	x
20	x	x	x	x	x	x	x	x	x
25	x	x	x	x	x	x	x	x	x
30	x	x	x	x	x	x	x	x	x
35	x	x	x	x	x	x	x	x	
40	x	x	x	x	x	x	x		
45	x	x		x	x	x			
50	x	x							

OmyaCarb UF

TiO$_2$	0	5	10	15	20	25	30	35	40
0	x	x	x	x	x	x	x	x	x
5	x	x	x	x	x	x	x	x	x
10	x	x	x	x	x	x	x	x	x
15	x	x	x	x	x	x	x	x	x
20	x	x	x	x	x	x	x	x	x
25	x	x	x	x	x	x	x	x	x
30	x	x	x	x	x	x	x	x	x
35	x	x	x	x	x	x	x	x	
40	x	x	x	x	x	x	x		
45	x	x	x	x	x	x			
50	x	x	x						
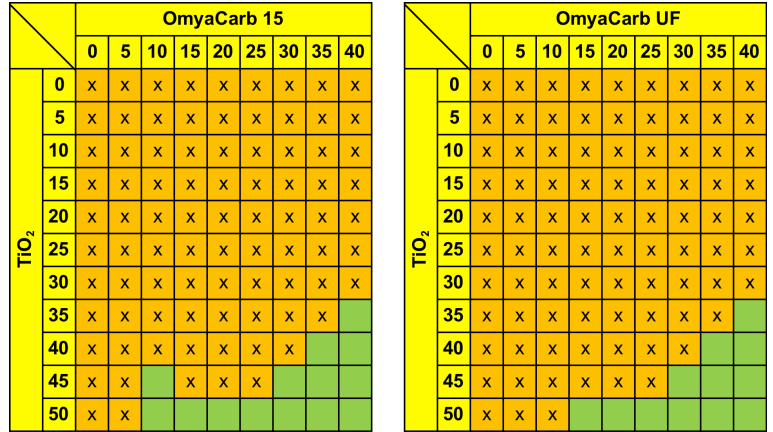
Figure 14: Visual Representation of Paint Samples Made

White paints were formulated into PVC ladders as 3-component systems which contained TFW-182 with Acrysol RM-8W (masterbatch), R-746 TiO$_2$ slurry, and either Omyacarb 15 or Omyacarb UF (extender) slurry. Additionally, white paints in 2-component systems were made in conjunction for use as reference systems which contained the modified masterbatch and either TiO$_2$ or CaCO$_3$ slurry. These PVC ladders were formulated with varying PVC levels of TiO$_2$ and/or CaCO$_3$ (pigments), but can be thought of as TiO$_2$ PVC ladders while keeping extender concentration constant. Additional PVC ladders were made with masterbatch and one pigment (R-746, R-741, Omyacarb 15, and Omyacarb UF. It is important to mention that PVC is an alternative notation for concentration, and that PVC itself can refer to the pigment and/or extender. Presented in Figure 14 is a visual representation of the paint or coating samples that were made. Boxes marked in orange indicate the TiO$_2$ and/or CaCO$_3$ PVC used for each

sample. The PVC for a each particular formulation is the sum of the Omyacarb and TiO_2 PVC values.

Paints were formulated to 50 mL or 100 mL samples in 2 oz or 4 oz glass jars, respectively. Jars were first filled in the following order: masterbatch, TiO_2 slurry, and finally the extender slurry. The glass jars were sealed with a lid and a plastic seal, placed between the jar opening and lid to prevent the paint from settling around the lid. Samples were placed in a Red Devil Shaker and shaken 10 minutes each side to ensure mixture of the paints for a total time of 20 minute shaking per paint sample. Density was measured for each paint sample and weight solids were obtained periodically to compare to calculated values.

5.3 Spread Rate Procedure

5.3.1 Weighed Drawdown

Weighed drawdowns were prepared to measure the performance of each paint sample. Paint sample drawdowns were prepared in replicates of 4 for each paint sample. Drawdowns were performed on an automatic drawdown machine with a drawdown bar film applicator with a thickness of 4 mils (0.004 inches) on special cut Leneta Opacity 14-H charts. Each Leneta chart contains 2 sets of alternating white and black backgrounds, giving a total of 4 squares. Paints were stirred slowly with a pipette prior to each drawdown, and then applied onto the Leneta chart with the paint pushed into the end of the drawdown bar. The paint was pushed to the far end of the drawdown bar to ensure the paint coverage area on each Leneta chart were similar to one another, having covered an area of 54.25 in^2 per drawdown. Additionally, each drawdown was individually

weighed, such that drawdowns for each paint sample were within ± 0.05 grams of each

other and left to dry overnight in the horizontal position for further analysis.

5.3.2 Contrast Ratio Measurements

A Hunterlab LabScan XE Spectrophometer loaded with Hunterlab Easymatch QC

Software 3.9.0 was used to measure the light reflectance of the drawdowns to obtain their

contrast ratio values. A 44 mm port size was used under D65 illuminant when obtaining

measurements. The Y tristimulus values were used to measure the reflectance values over

the black and white backgrounds. Together, these values determine the contrast ratio for

the dry paint. The reflectance of the special cut Leneta Opacity 14-H charts were taken

into account by measuring the reflectance over the white background of 8 randomly

selected charts per box.

Contrast ratio was measured for the drawdowns that were left overnight to dry

from the previous day by measuring the light reflectance values or Y tristimulus value of

the coating over the black and white backgrounds. One measurement was made for each

of the 4 backgrounds per opacity chart – 2 values each for the black and white

backgrounds for each drawdown for the particular paint. The Y tristimulus values were

averaged for each black and white substrate

Additional contrast ratio measurements were performed towards the end of the

ladder study to determine whether or not the formulated paint was above CPVC.

Drawdown charts were coated with mineral oil with a paint roller over the drawdown and

left to level horizontally for 20 minutes. Oiled contrast ratio measurements were obtained

in the same manner by measuring the light reflectance over the black and white

backgrounds and compared to previous measurements. Selection of drawdown charts was

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based on PVC ladders to which the CPVC range was not easily distinguished based on spread rate values. Due to the destructive nature of the oiled contrast ratio measurements, repeating of this test was avoided as necessary.

5.3.2 Spread Rate Calculation

The Spread Rate Program v2.1 (DuPont) was used to generate spread rate values for each paint sample. This program utilizes Kubelka-Munk relationships to extrapolate and interpolate the X value. Input variables needed to calculate spread rate include the paint density, TiO_2 content, reflectance over white, reflectance over black, substrate reflectance, drawdown weight, and drawdown coverage area. The TiO_2 content was calculated based on the quantity of slurry added and the volume of paint made for each paint sample. Output data of concern is the spread rate value at complete hiding. Shown in Figure 15 is a screenshot of the Spread Rate Program used to calculate the spread rate for the measured paint samples. Additional output data, such as actual scattering (S) and thickness (X) values for the drawdowns as is as and S and X values extrapolated at complete hiding are provided. Additionally, there is an additional parameter to calculate these values at R_∞. For simplicity and practical application, the additional output data is not used for the purposes of this study.
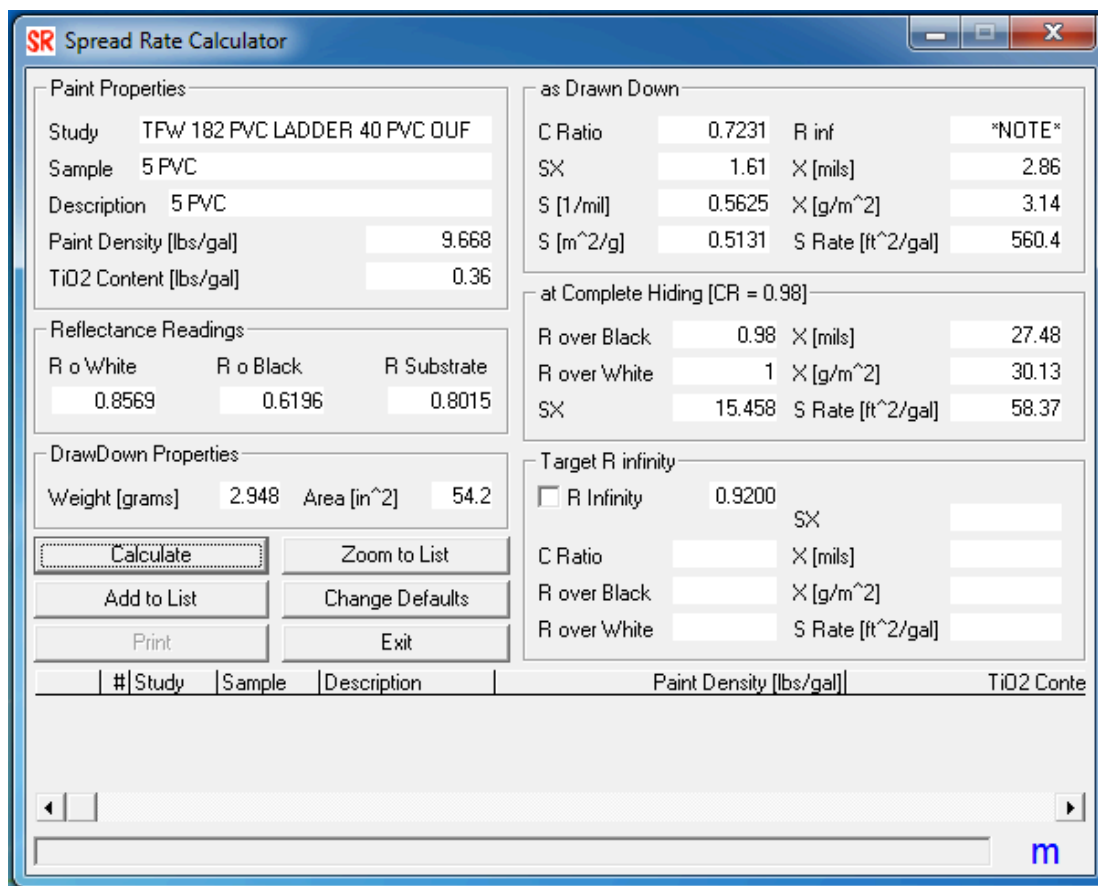
Figure 15: Spread Rate Program v.2.1 (DuPont) Screenshot

Scatter plots were generated using a combination of the contrast ratio and spread rate values against total PVC. A statistical package, Origin Pro v9, was used to model best fit lines and polynomials in order to find estimated CPVC values. Additional oiled contrast ratio tests were performed to ascertain whether a particular PVC value was above or below CPVC for each paint system (at constant $CaCO_3$ PVC).

5.4 Oil Absorption

Oil absorption tests were also performed for TiO_2 and $CaCO_3$ pigment grades used in the slurry solutions. These oil absorption (OA) values are another way to determine relative CPVC values of a pigment system. OA tests were performed using the

R-706 and R-931 pigment grades of TiO_2 and Omyacarb UF and Omyacarb 15 pigment

grades of $CaCO_3$. Additional OA tests were performed with pigment blends containing R-

706 with Omyacarb UF and 15.

Oil absorption tests were performed according to ASTM Method D281-12,

Standard Test Method for Oil Absorption of Pigments by Spatula Rub-Out. Oil

absorption tests were performed in triplicates for each pigment sample. Pigment was

weighed out in varying amounts (between 1-2 grams) on waxed weighing paper and

placed on a glass plate. A burette was filled with linseed oil and added to the pigment

sample in a drop wise manner. A spatula was used to incorporate the linseed oil into the

pigment. The OA test for each sample was complete when enough oil was applied to and

incorporated into the pigment sample with a consistency of a stiff, putty-like paste that

does not break or separate. The volume of linseed oil required to wet the pigment was

recorded, with pigment mass taken into account to obtain an OA value. A different

quantity of pigment was used for each subsequent OA test to test for repeatability. OA

values are constant, ignoring flocculation effects, thus OA tests with different quantities

of pigment should provide similar OA values.

5.4.1 Blend Preparation

Pigment blends were prepared for $TiO_2/CaCO_3$ pigment mixtures. Pigments used

for blending include R-706 TiO_2 with Omyacarb 15 and Omyacarb UF $CaCO_3$ separately.

Pigments were added appropriately into a test tube as 5 gram pigments blends, scaled to

volume ratios shown in Table 10. Test tubes were sealed with parafilm. Blending or

mixing of the pigments were performed by shaking and tapping the test tube for

approximately 2 minutes each.

Table 10: Pigment Blend Formulations

Volume %		Mass (g)	
Omyacarb 15	**R-706**	**Omyacarb 15**	**R-706**
0%	100%	0.00	5.00
20%	80%	0.71	4.29
40%	60%	1.53	3.47
60%	40%	2.48	2.52
80%	20%	3.62	1.38
100%	0%	5.00	0.00
Volume %		**Mass (g)**	
Omyacarb UF	**R-706**	**Omyacarb UF**	**R-706**
0%	100%	0.00	5.00
20%	80%	0.71	4.29
40%	60%	1.53	3.47
60%	40%	2.48	2.52
80%	20%	3.62	1.38
100%	0%	5.00	0.00

6. Results and Discussion

6.1 Contrast Ratio

Table 11: Averaged Contrast Ratio – Omyacarb 15 (a) and Omyacarb UF (b)

		Omyacarb 15 PVC								
		0	5	10	15	20	25	30	35	40
R-746 PVC	0	0.022	0.031	0.035	0.041	0.046	0.052	0.055	0.068	0.088
	5	0.815	0.727	0.713	0.723	0.711	0.737	0.695	0.669	0.649
	10	0.906	0.853	0.846	0.840	0.814	0.825	0.797	0.771	0.756
	15	0.909	0.892	0.890	0.883	0.862	0.858	0.829	0.815	0.805
	20	0.926	0.914	0.902	0.899	0.877	0.867	0.847	0.841	0.842
	25	0.936	0.920	0.912	0.904	0.886	0.876	0.873	0.882	0.889
	30	0.940	0.925	0.913	0.900	0.892	0.897	0.900	0.912	0.932
	35	0.940	0.922	0.918	0.917	0.920	0.926	0.929	0.935	
	40	0.939	0.929	0.936	0.938	0.942	0.946	0.948		
	45	0.953	0.948		0.959	0.957	0.956			
	50	0.965	0.960						Above CPVC	

(a)

		Omyacarb UF PVC								
		0	5	10	15	20	25	30	35	40
R-746 PVC	0	0.022	0.024	0.031	0.043	0.054	0.075	0.095	0.103	0.138
	5	0.815	0.725	0.720	0.718	0.724	0.714	0.719	0.706	0.723
	10	0.906	0.849	0.846	0.842	0.840	0.822	0.824	0.861	0.866
	15	0.909	0.894	0.892	0.890	0.885	0.870	0.885	0.898	0.928
	20	0.926	0.916	0.911	0.908	0.902	0.910	0.918	0.933	0.952
	25	0.936	0.921	0.921	0.917	0.913	0.935	0.943	0.954	0.959
	30	0.940	0.928	0.924	0.928	0.937	0.954	0.959	0.965	0.967
	35	0.940	0.926	0.931	0.945	0.954	0.966	0.968	0.973	
	40	0.939	0.938	0.951	0.960	0.965	0.971	0.971		
	45	0.953	0.953	0.975	0.968	0.971	0.975			
	50	0.965	0.966	0.981					Above CPVC	

(b)

The reflectance values of the paints over a black and white substrate are the basis for the values in this report. As a quotient, these values give the contrast ratio for the prepared paint samples. The contrast ratio value, averaged from the drawdowns, for each pigment combination at formulated concentrations is presented in Table 11. Two types of

pigments – TiO$_2$ (R-746) and CaCO$_3$ (Omyacarb 15 and Omyacarb UF) were used in the paint system. It is reasonable in wanting to know which pigment is responsible in the increase of the contrast ratio for hiding purposes. Going down each column corresponds to an increase in TiO$_2$ PVC and across each row an increase in CaCO$_3$ PVC for each Omyacarb grade.

The general observable trend is that the contrast ratio increases with increasing PVC regardless of the pigment type. For each PVC ladder, the increase to 5 PVC TiO$_2$ resulted in an increase of the contrast ratio from close to 0 to at least 0.60. These results indicate that TiO$_2$ has dramatic effect in influencing the contrast ratio compared to CaCO$_3$. There are some instances where an increased concentration lowers the contrast ratio regardless of pigment type added, which are due to crowding effects.

Highlighted values indicate samples above CPVC. The CPVC cutoff point was determined visually through extrapolation of spread rate values (Section 6.2). Oiled contrast ratio measurements were performed at high PVC due to the difficulty in determining the CPVC cutoff point. A paint formulation was determined to be above PVC if there was a difference between the oiled and unoiled contrast ratios. This is due to the air voids being filled in with oil if above CPVC. The particular contrast ratio differences are provided in Appendix A: Oiled Contrast Ratios.

The contrast ratios for the drawn down paint samples containing Omyacarb 15 can also be visually represented with the plot in Figure 16. The contrast ratio is plotted as a function of TiO$_2$ (R-706/R-746) and Extender (Omyacarb 15) PVC. A similar plot was made for Omyacarb UF, providing similar results is provided for reference in Appendix B: Pigment Contrast Ratio Plot. As mentioned from the data from Table 11, the contrast

ratio dramatically increases at increasing TiO_2 PVC. The increase is due to the high

refractive index of TiO_2. The values at 0 TiO_2 PVC represent the contrast ratios of

masterbatch itself and of the extenders. At each particular PVC value, there is a small

range in the contrast ratio, which shows dependence, especially when compared to that of

the extender. The narrow range indicates that the contrast ratio can potentially be

modeled as a function of TiO_2 PVC.
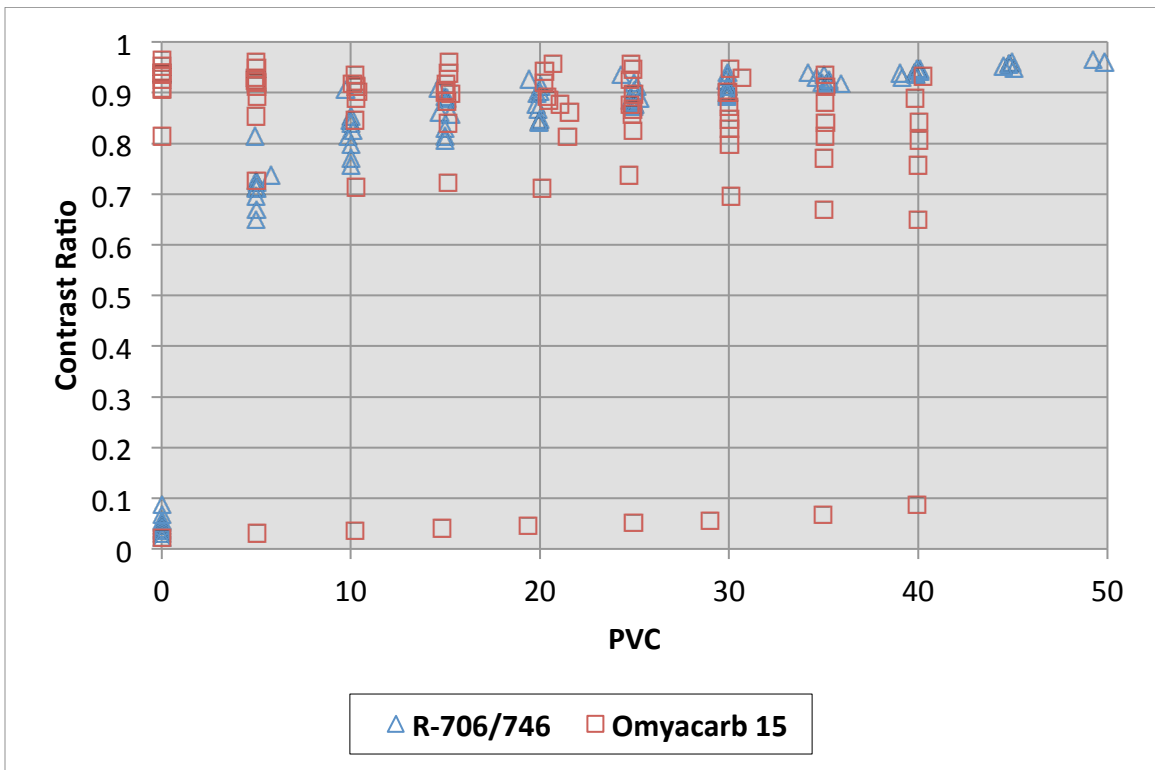
Figure 16: Contrast Ratios with Paints containing Omyacarb 15

There are few arguments to support that the contrast ratios depends on the

extender PVC. The main point being that there is a dramatic range of contrast ratios at

each PVC value. Even if the contrast ratio values below 0.50 are ignored, the contrast

ratio range increases at increasing PVC. The only distinctive trend is at low contrast ratio.

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These values contain no TiO_2 and gradually increase. This large range indicates that the contrast ratio is sensitive to the TiO_2 concentration.

6.2 Spread Rate

The primary question is to consider the effects of Omyacarb on the light scattering properties of TiO_2. Since the scattering value, S, derived from Kubelka-Munk relationships is not necessarily representative of practical performance; spread rate values are used as a means to measure the degree of light scattering.

6.2.1 TiO_2 grades

Spread rate defined in this context the area coverage in square feet for a gallon of paint. The actual spread rate values are derived from Kubelka-Munk relationships, which are then extrapolated to complete hiding, which is a contrast ratio of 0.98. Spread rates values were plotted for two grades of TiO_2 (R-746 and R-741) in Figure 17 and modeled as a function of PVC. In this case, TiO_2 and total PVC are equal to one another. It is unsurprising that both plots exhibit similar features to that of the example in Figure 12. The spread rate models can be broken into 2 functions - a parabolic function up to CPVC and linear function above CPVC. The parabolic function relates to the TiO_2 crowding effects and the linear function relates to the presence of air voids. The spread rate values for R-746 are greater than R-741 below CPVC due to the higher TiO_2 content. At 5 PVC, the spread rate values are nearly identical to one another despite the fact R-741 contains less TiO_2. This point is not believed to be an outlier, but a limitation of the parabolic model. R-741 pigments have a porous surface as a result of the surface treatment performed. As a result, crowding effects are reduced due to the 'thick' shell, which increases the interparticle distance of the TiO_2 compounds. The impact of increased

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interparticle distance is that the scattering efficiency increases, which is reflected upon the spread rate.
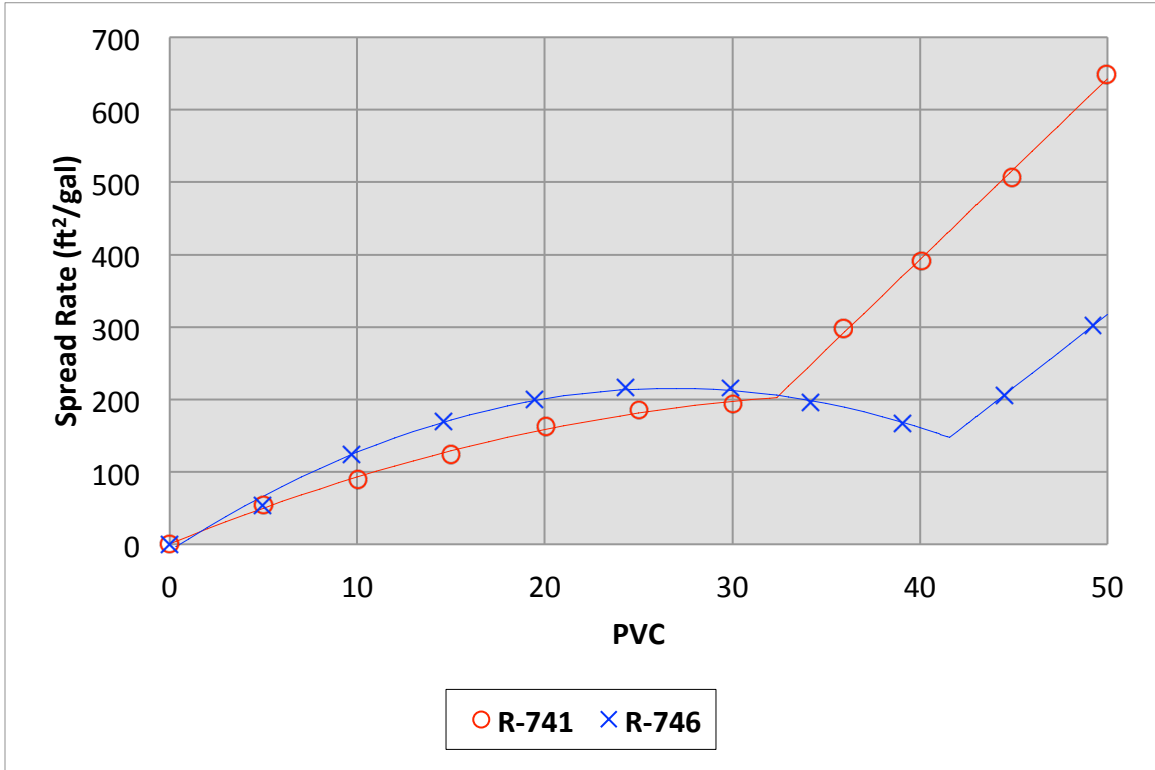
Figure 17: Spread Rate Comparison between TiO$_2$ grades

The CPVC for R-741 is much lower than expected, as larger particles tend to have higher CPVC values. The thick shell implies that the actual TiO$_2$ particle is smaller than it appears. Again, since the shell is porous, the density is concentrated towards the center of the particle. OA tests and surface area relationships are additional explanations to account for this. Above CPVC, spread rate increases linearly for both TiO$_2$ grades due to the presence of air voids.

In addition to coverage area, the spread rate can be though of in terms of a volume basis. For a given area, a paint providing greater spread rate requires less volume. The spread rate plots throughout this paper are not necessarily indicative of spread rates in

commercial paints. Rheological factors were not considered in this study, but are believed to influence spread rate values, especially at high PVC levels due to the low volume solids (21.5%), which affect the dispersion of the pigments in the paint system.

6.2.2 Total PVC – Omyacrab 15

Spread Rate values and models for samples containing Omyacarb 15 are presented relative to the Total PVC (combination of TiO_2 and $CaCO_3$) in Figure 18. Each curve or model represents a PVC ladder at constant Omyacarb 15 concentration with increasing R-746 concentration. Additionally, interpolated CPVC values are indicated in the figure, based on the intercept of the modeled polynomial and linear functions for each model. The data is plotted relative to Total PVC to study the impact of additional extender to the entire paint system. At low Omyacarb 15 replacement, determination of spread rate values being above or below CPVC was done visually through data comparison. At high Omyacarb 15 replacment, oiled contrast ratio measurements were performed.

It is unsurprising for the most part that spread rates are lower for paints with greater Omyacarb 15 content at a constant Total PVC. This is because TiO_2 is replaced with Omyacarb 15 on a volume basis at Total PVC. Since TiO_2 is responsible for the increase in the spread rate due to its light scattering ability, it makes sense that less TiO_2 results in a lower spread rate.
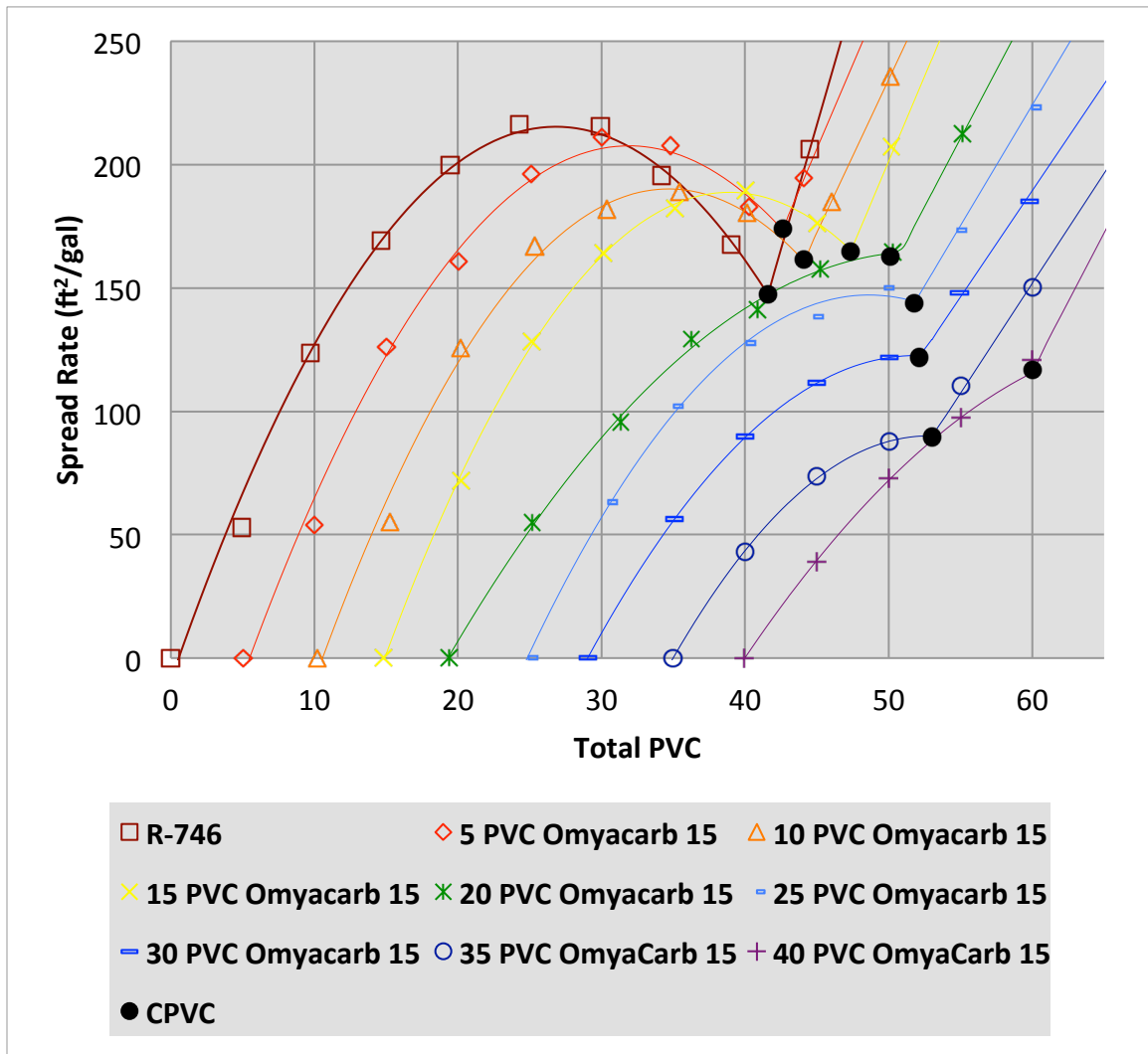
Figure 18: Spread Rate of PVC Ladders containing Omyacarb 15

In the 30-45 PVC range however, there is some overlap in the spread rate values among the models, deviating from the trend. Roughly 15 PVC TiO_2 can be with Omyacarb 15 with comparable if not better spread rate values, just below CPVC. Do note that only spread rate is considered in this analysis. Crowding effects of TiO_2 particles has been diminished with partial replacement with Omyacarb 15, while retaining enough TiO_2 for light scattering. The replacement of TiO_2 particles by a larger particle does not necessarily result in the same volume displacement. Packing efficiency is not 100%,

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which results in the presence of voids. As a result, the TiO$_2$ particles can be thought of as being spaced far enough such that crowding effects are marginally minimized, which can account for the slight increase in spread rate.

Table 12: Omyacarb 15 Replacement CPVC Values

Omyacarb 15 PVC	0	5	10	15	20	25	30	35	40
CPVC	41.6	42.6	44.1	47.3	50.1	51.8	52.1	53.0	60.0

There is a distinct trend in the CPVC values with increased Omyacarb 15 PVC. The actual values are presented in Table 12. This is the result of the packing dynamics of the pigments due to their size difference. Omyacarb 15 is significantly larger than TiO$_2$ pigments used in paint. The difference in size enables TiO$_2$ pigments to pack in the interstitial sites allowing for more packing – increasing available surface area, which results in higher CPVC. The decrease in spread rate is the result of added extender, which itself does not contribute to hiding. Additionally, the packing of TiO$_2$ particles in the interstitial sites can also undergo crowding, which lowers the scattering efficiency of each TiO$_2$ particle.

6.2.2 Total PVC – Omyacrab UF

Spread Rate values and models for samples containing Omyacarb UF are presented relative to the Total PVC in Figure 19. This graph was plotted in a similar manner to that of Omyacarb 15 in Figure 18. Determination of whether a spread rate was above or below CPVC was performed in a similar manner as mentioned for Omyacarb 15.
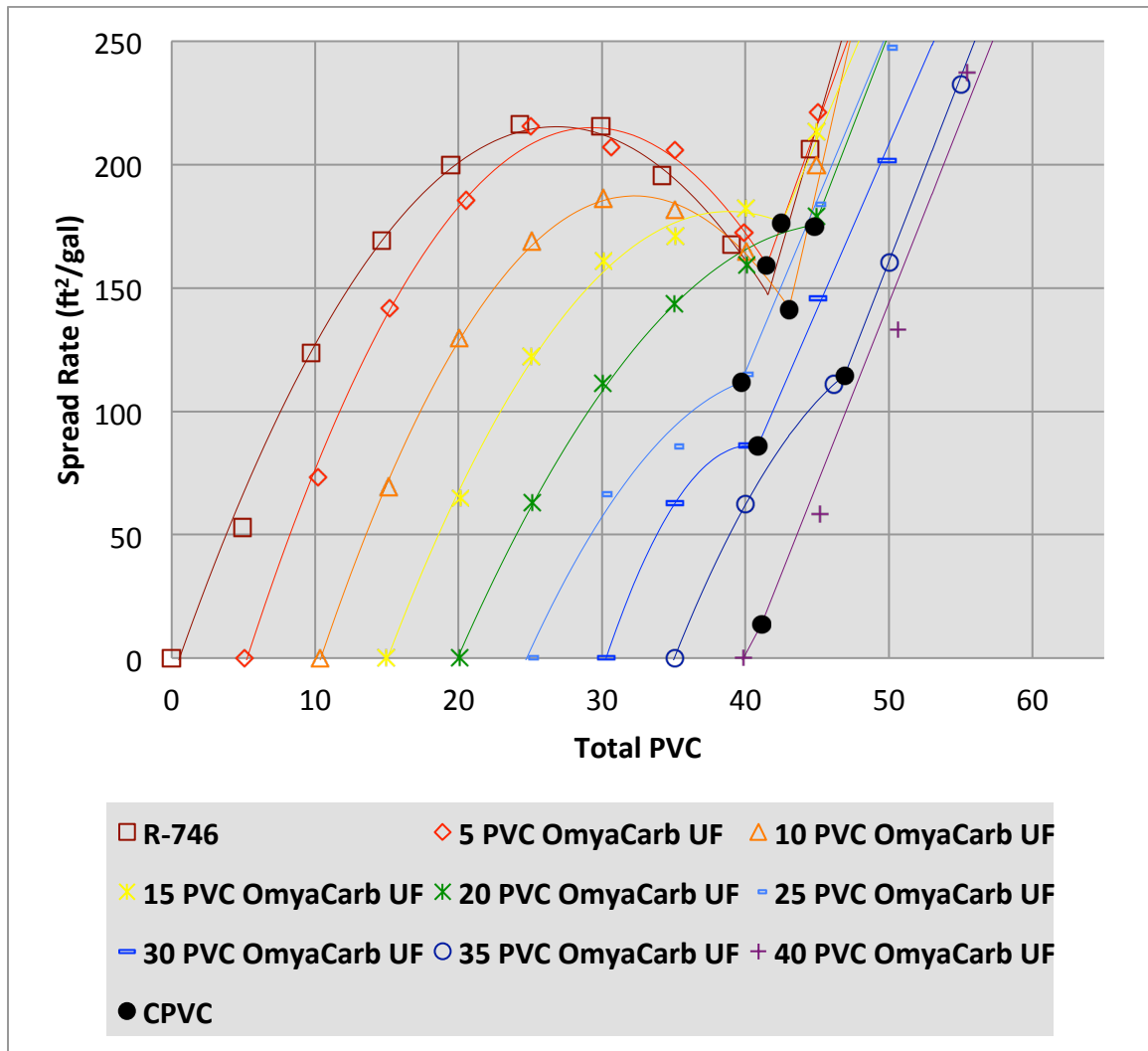
Figure 19: Spread Rate of PVC Ladders containing Omyacarb UF

Similar to the results with Omyacarb 15, an increase in Omyacarb UF PVC generally lowers the spread rate at when at a constant total PVC. One subtle difference with the model (plot) overlaps for Omyacarb UF, are that they are slightly more exacerbated. This is because the particle size difference is not as pronounced between the TiO$_2$ (0.36 μm) and Omyacarb UF (0.70 μm) particles compared to that of Omyacarb 15 (15 μm). The likelihood of crowding in the interstitial sites of Omyacarb UF is lower as the void size is unable to accommodate multiple TiO$_2$ particles without displacement of

the extender particles. This allows for a more uniform dispersion of the TiO_2 particles to reduce crowding effects, which can explain the increase of spread rate with lower TiO_2 concentration. The replacement of up to 20 PVC Omyacarb UF below CPVC is rather significant, especially when considering the cost of TiO_2.

Table 13: Omyacarb UF Replacement CPVC Values

Omyacarb UF PVC	0	5	10	15	20	25	30	35	40
CPVC	41.6	41.5	43.0	42.5	44.8	39.7	40.9	46.9	41.1

The CPVC range with for the paint sample containing Omyacarb UF presented in Table 13 are similar to one another unlike Omyacarb 15. Omyacarb UF is of the same size order of typical TiO_2 pigment particles. Omyacarb UF essentially replaces TiO_2 on a particle basis compared to Omyacarb 15. The sizes of the void spaces are significantly smaller, which minimize the ability of TiO_2 particles to fit and pack in them. As a result, crowding within the voids is unlikely, giving virtually no change to the surface area, which is the result of little to no change in the CPVC.

6.2.4 Consideration of TiO_2 PVC

Simply stating that the spread rate decreases with additional extenders is misleading. Analysis so far was based on the total PVC. Omyacarb itself contributes little to the increase in spread rate, but influences the spread rate when used in conjunction with TiO_2. The particular spread rate values are broken down to the particular concentrations of TiO_2 and various Omyacarb grades in Table 14. Spread rate values above CPVC are highlighted because an additional mechanism contributes to the spread rate. Considering the differences in spread rate at constant TiO_2 PVC gives a better

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understanding of light scattering solely due to TiO2. Addition of Omyacarb for the most part did not improve the spread rate below CPVC. The initial addition of Omyacarb at low TiO_2 concentration actually increased the spread rate. The increase is marginal for Omyacarb 15, but is more significant for Omyacarb UF. Again, this relates to alleviation of crowding as Omyacarb acts as spacers to extend the TiO_2 interparticle distance to increase scattering efficiency. This reasoning can also explain why addition of Omyacarb UF results in a greater spread rate than Omyacarb 15. Spread rate plots comparing Omyacarb UF and Omyacarb 15 are provided in Appendix C: Comparison of Spread Rate Plots with Omyacarb Grades.

Table 14: Spread Rate Values – Omyacarb 15 (a) and Omyacarb UF (b)

R-746 PVC		Omyacarb 15 PVC								
		0	5	10	15	20	25	30	35	40
	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	5	53.08	54.11	55.03	72.12	54.80	63.18	56.20	43.05	38.94
	10	123.57	126.13	125.78	128.32	95.79	102.34	89.94	73.62	72.83
	15	169.19	160.91	166.97	164.15	129.38	127.64	111.50	87.67	97.30
	20	200.11	196.06	181.88	182.29	141.27	138.25	121.73	110.44	120.82
	25	216.59	210.99	188.88	189.76	157.79	149.84	148.10	150.28	164.41
	30	215.56	207.76	180.51	176.29	164.55	173.37	185.10	193.55	233.88
	35	195.59	182.86	184.85	207.55	212.31	223.24	234.01	244.69	
	40	167.59	194.66	235.91	262.51	268.92	276.03	277.72		
	45	206.18	272.88		344.68	326.72	316.81			
	50	301.34	342.08						Above CPVC	

(a)

R-746 PVC		Omyacarb UF PVC								
		0	5	10	15	20	25	30	35	40
	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	5	53.08	73.28	69.36	64.80	63.13	66.27	62.80	62.60	58.37
	10	123.57	141.61	129.75	122.38	111.35	85.72	86.12	110.89	133.27
	15	169.19	185.44	168.98	161.03	143.56	115.12	145.87	160.27	237.28
	20	200.11	215.56	186.29	170.97	159.52	184.02	201.49	232.41	319.79
	25	216.59	207.23	181.56	182.37	179.00	247.52	271.43	315.58	359.91
	30	215.56	205.87	164.68	213.42	250.25	324.63	356.44	387.28	423.07
	35	195.59	172.34	200.11	272.70	329.89	410.70	417.86	454.20	
	40	167.59	221.18	295.23	347.03	412.78	473.19	455.72		
	45	206.18	289.56	473.19	414.88	475.40	525.02			
	50	301.34	382.19	563.50					Above CPVC	

(b)

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6.2.5 Particle Size Effects on Resin Demand

The paints can be thought of as a 3-part system, represented as a contour plot to relate the spread rate values at varying concentrations of the components. These contour plots for a 3-component system are typically referred to as contour ternary plots. CPVC values can also be compared throughout the PVC ladders to examine the impact of material demand as they are replaced with one another. In this case CPVC values can be compared together to determine the effect on resin demand.
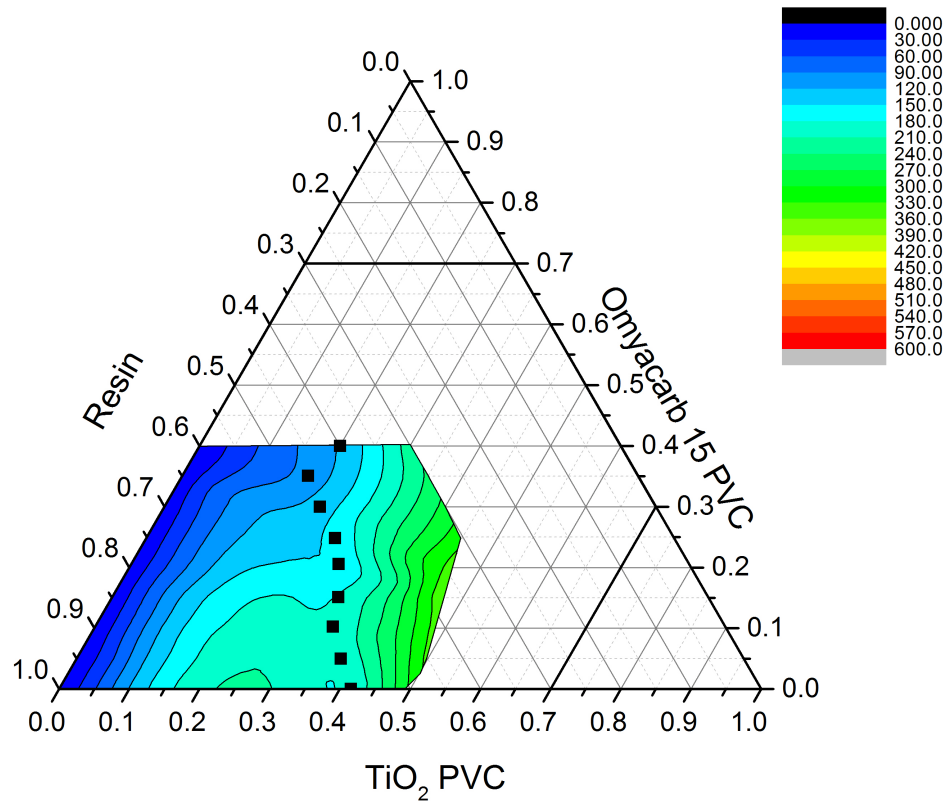
Figure 20: Omyacarb 15 Spread Rate Ternary Plot

The ternary plot with Omyacarb 15 is presented in Figure 20. Increasing PVC of Omyacarb 15 results in a lower resin demand. This can be explained again with packing

of TiO$_2$ particles within the interstitial voids created with the larger Omyacarb 15

particles. Within these voids, TiO$_2$ particles can undergo crowding effects, which results

in the lower spread rates compared to Omyacarb UF. Oil absorption tests support this

argument and data. The decreased resin demand has provides a means to reduce materials

cost as Omyacarb 15 is cheaper than the resin and TiO$_2$.
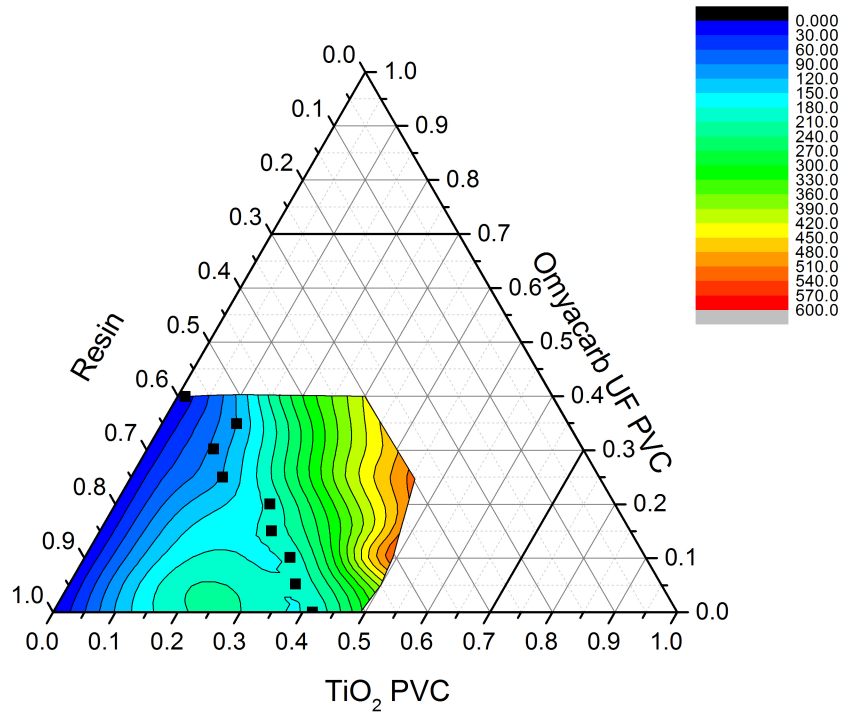
Figure 21: Omyacarb UF Spread Rate Ternary Plot

The ternary plot with Omyacarb UF is presented in Figure 21. Increasing

Omyacarb UF PVC results in little to no change in resin demand. Again, since Omyacarb

UF and the TiO$_2$ particles are on the same size order, there is little change in volume

when they are replaced with one another, thus resulting in little to no change in the resin

demand. Unlike Omyacarb 15, there is no change in resin demand with small particles.

When spread rate is taken into account however, increases are marginal to significant, especially at low TiO_2 concentrations.

6.3 Oil Absorption

Table 15: Particle OA Values

Particle	Particle Size (μm)	OA Value
R-706 (R-746)	0.36	28
R-931 (R-741)	0.55	45
Omyacarb UF	0.70	36
Omyacarb 15	15.0	19

The OA values for the TiO_2 and Omyacarb particles are listed in Table 15. The general relationship between OA and particle size is that smaller particles have higher OA values resulting from the increased surface area to volume ratios. This relationship between the TiO_2 and $CaCO_3$ pigments was considered separately due to the different chemistries of the particles, which can drastically alter the OA value.

These OA tests were performed on a volume basis then converted to mass, which may have led to inaccurate OA values due to the quantity of pigment used for each test. Regardless of the accuracy of the data, the trends and relationships were of more significant concern to reaffirm the trends exhibited in the spread rate graphs.

The OA values for the different TiO_2 particles do not follow the general trend. In the R-931 case, there is a fluffy alumino-silicate surface treatment, which can be though of as a partially porous surface treatment, which actually increases the surface area, causing the OA values to exceed what is expected. Omyacarb OA values conformed to the general relationship as the smaller Omyacarb UF particles was shown to have higher OA values.
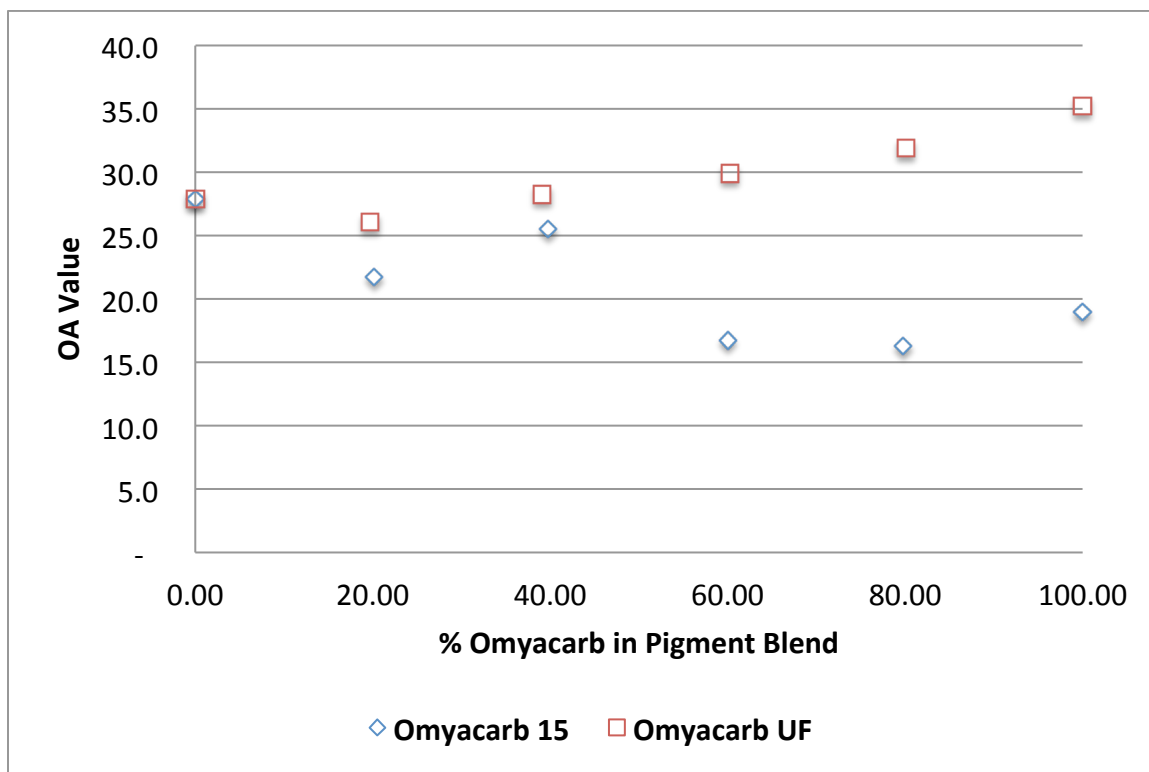
Figure 22: Pigment Blend OA Values

OA Values for the R-706/Omyacarb 15 and R-706/Omycarb UF pigment blends are plotted in Figure 22. Pigment blends containing Omyacarb 15 have particle sizes differences by an order of magnitude whereas blends containing Omyacarb UF have particle sizes on the same order of magnitude.

The Omyacarb UF pigment blend overall has a linear or close to linear relationship to its OA value. Since the particles are on the same size order, there is close to equal replacement of the particles with little to no displacement of the linseed oil. The slight increase in the OA value is result the different materials use in the pigment blend. When these OA values are converted to their CPVC values, they follow a similar trend to the modeled CPVC values. Both cases show little to no change in the CPVC values. The

initial data point is considered an outlier in this situation due to limitations and variation of obtaining OA values by volume.

The Omyacarb 15 pigment blend does not appear to exhibit a linear relationship. The 40% Omyacarb 15 data point is considered an outlier. Since the Omyacarb 15 particles are significantly larger in comparison to R-706, the TiO_2 particles are able to fit freely in the voids and undergo packing. This void space is therefore occupied when performing OA tests; lowering OA values. This trend is also reaffirmed when OA values are converted to CPVC values, which increase under both cases.

7. Conclusion

The goal of this study was to examine the effect of different sized $CaCO_3$ particles on TiO_2 light scattering in coatings. Light scattering can be represented in terms of the contrast ratio and spread rate for each particular paint formulation. The contrast ratio is a direct means to measure light reflectance off a surface, which can result from light scattering off particles in the dry paint. As expected, TiO_2 scatters light more than $CaCO_3$ when comparing the contrast ratio. Replacement of TiO_2 with $CaCO_3$ reduces the contrast ratio as a result.

The DuPont Spread Rate Program is built upon Kubelka-Munk relationships, which allows extrapolation and interpolation of paint performance at complete hiding. Replacement of TiO_2 with resin increases the spread rate of a paint formulation, but only at low levels. Additionally replacement of TiO_2 with $CaCO_3$ results in greater spread rate right under CPVC. When comparing replacement with the different Omyacarb grades, the increase is marginal with Omyacarb 15, but rather significant with Omyacarb UF. The initial increase is due to reduced crowding effects among the TiO_2 particles as the Omyacarb particles act as spacers to extend the interparticle TiO_2 distance, improving scattering which can be expressed as spread rate. Too much Omyacarb 15 recreates crowding within the extender voids. Above CPVC, the spread rate dramatically increases due to the presence of air voids in between the pigment particles.

The CPVC values were extrapolated from the Spread Rate plots showing trends between similar and different sized calcium carbonate particles. Addition of large particles increases the CPVC value, whereas addition of similar sized particle results in

negligible changes in the CPVC. Again, this is due to the ability of the small particles fitting within the voids formed from the larger particle.

CPVC trends can also relate to the resin demand. Resin demand decreases with additional Omyacarb 15. If a volume of a large particle replaces many smaller particles such that the volumes are equal, they do not necessarily occupy the same space. There is no real significant change in resin demand with Omyacarb UF. This is due to a substitution of one particle for another, where both occupy roughly the same volume.

The CPVC extrapolations trends among the Omyacarb 15 and UF models can be checked against OA values involving pigment blends. OA values for Omyacarb UF blends correlate with a fairly linear relationship due to being similar sized to TiO_2. In the case of Omyacarb 15, the OA values decrease then marginally increase. Again, this is because the voids are big enough such that smaller particles are able to pack inside, displacing the linseed oil to lower the OA value.

This project report can be considered as a first study for the particular grades of TiO_2 and $CaCO_3$ used in this study. Additional PVC need to be made with nano-sized $CaCO_3$ extenders in a similar manner such that packing of TiO_2 can be studied with particles smaller than the pigment. PVC ladders were only made with the R-706 grade of TiO_2 and it would be interesting to see the results if a highly surface treated R-931 grade was used instead. Viscosity was ignored, but could be taken into account, especially at high PVC in future studies.

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Appendix A: Oiled Contrast Ratios

PVC		Contrast Ratio			Status
Omyacarb 15	R-746	Initial	Oiled	Change	Above/Below CVPC
20	30	0.8949	0.8816	0.0133	Below
20	35	0.9196	0.8874	0.0322	Above
25	25	0.8739	0.8618	0.0121	Below
25	30	0.8971	0.8740	0.0231	Above
30	20	0.8470	0.8313	0.0157	Below
30	25	0.8687	0.8454	0.0233	Above
35	15	0.8188	0.8029	0.0159	Below
35	20	0.8416	0.8208	0.0208	Above
40	15	0.8082	0.7906	0.0176	Below
40	20	0.8522	0.8080	0.0442	Above

PVC		Contrast Ratio			Status
Omyacarb UF	R-746	Initial	Oiled	Change	Above/Below CVPC
20	20	0.9019	0.8963	0.0056	Below
20	25	0.9158	0.9081	0.0077	Below
20	30	0.9370	0.9120	0.0251	Above
25	15	0.8701	0.8618	0.0083	Below
25	20	0.9110	0.8866	0.0244	Above
30	10	0.8220	0.8140	0.0080	Below
30	15	0.8836	0.8589	0.0246	Above
35	0	0.1032	0.0599	0.0433	Above (extender only)
35	5	0.7054	0.6831	0.0223	Below
35	10	0.8591	0.8317	0.0275	Below
35	15	0.8980	0.8545	0.0435	Above
35	20	0.9317	0.8832	0.0484	Above
40	0	0.1381	0.0721	0.0659	Above (extender only)
40	5	0.7224	0.6860	0.0364	Below
40	10	0.8691	0.8062	0.0629	Above
40	15	0.9310	0.8676	0.0635	Above

Appendix B: Pigment Contrast Ratio Plot
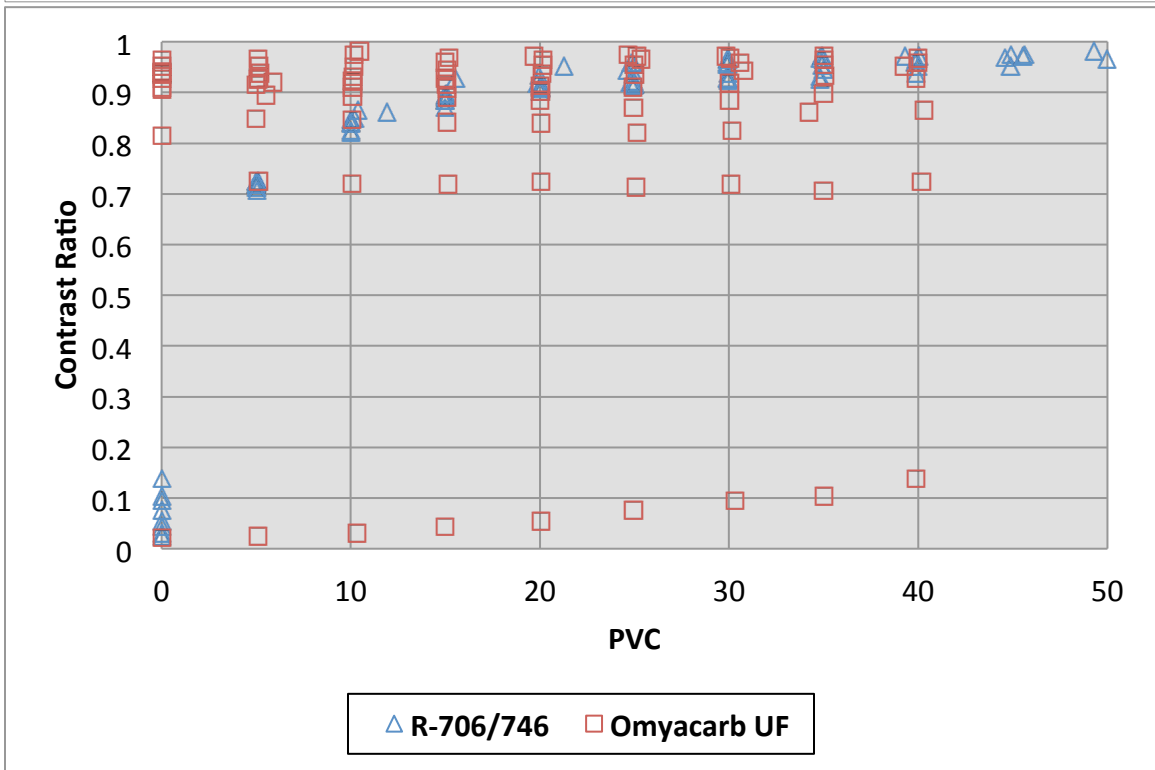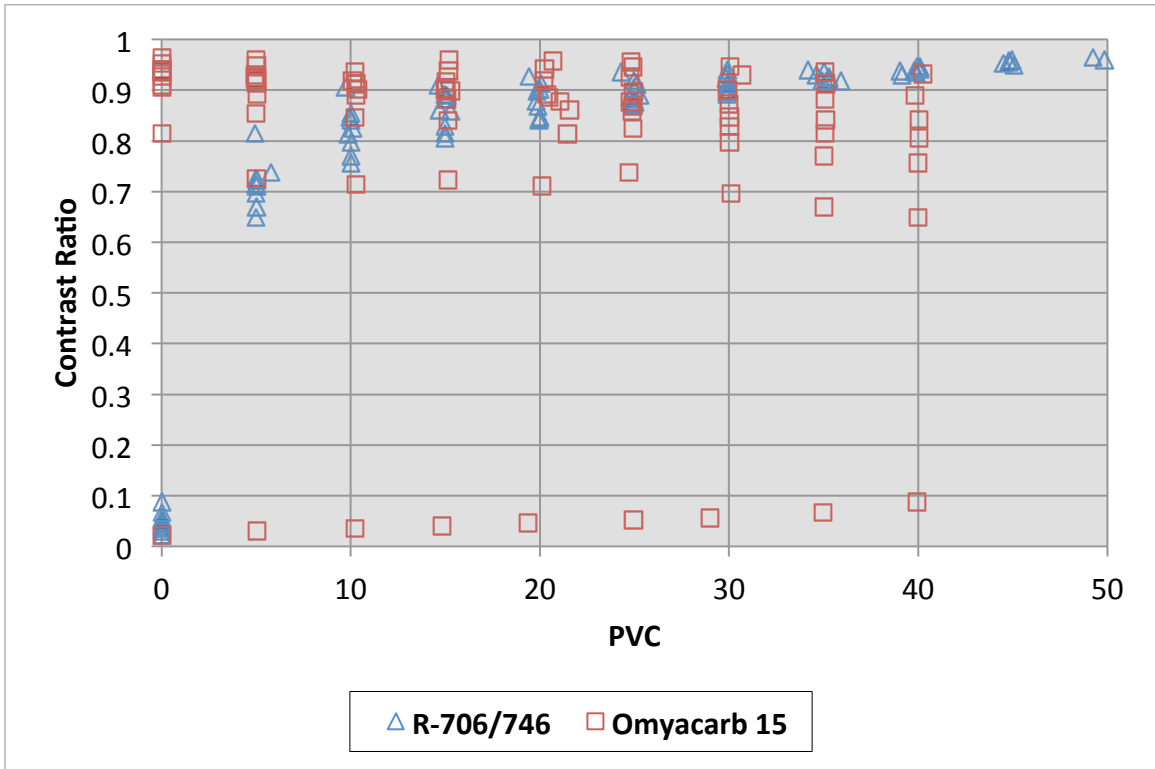
Appendix C: Comparison of Spread Rate Plots with Omyacarb Grades
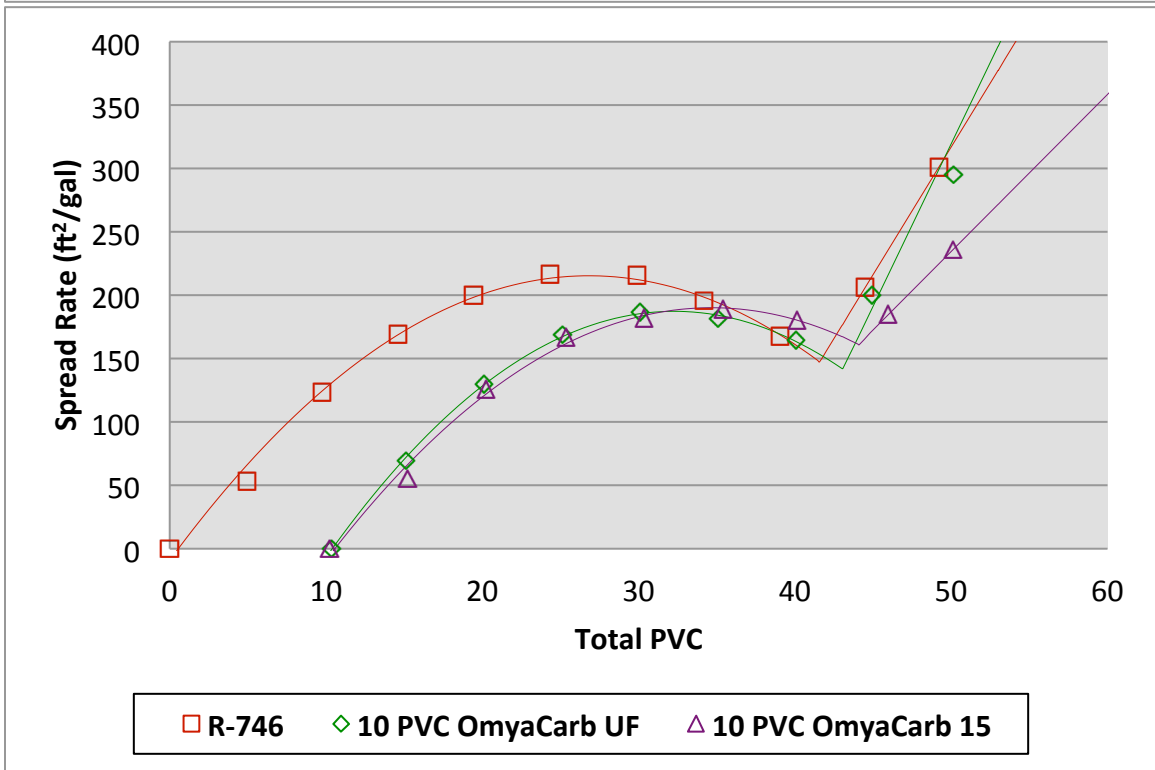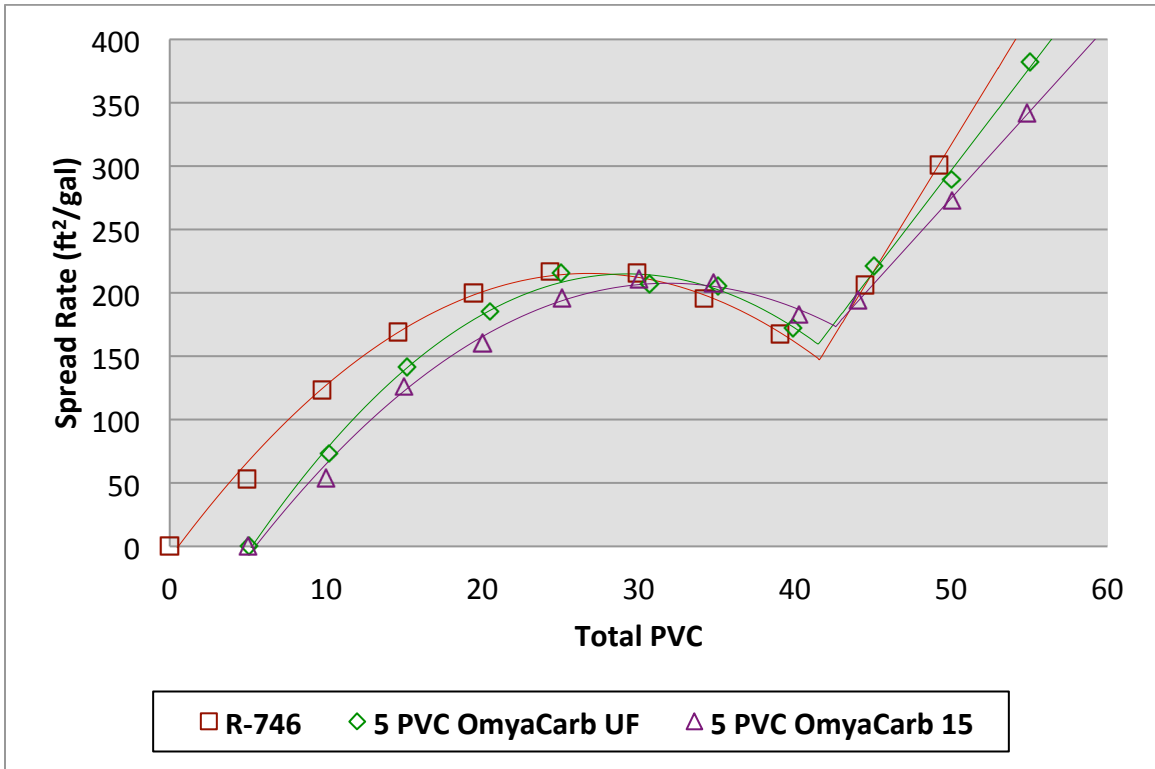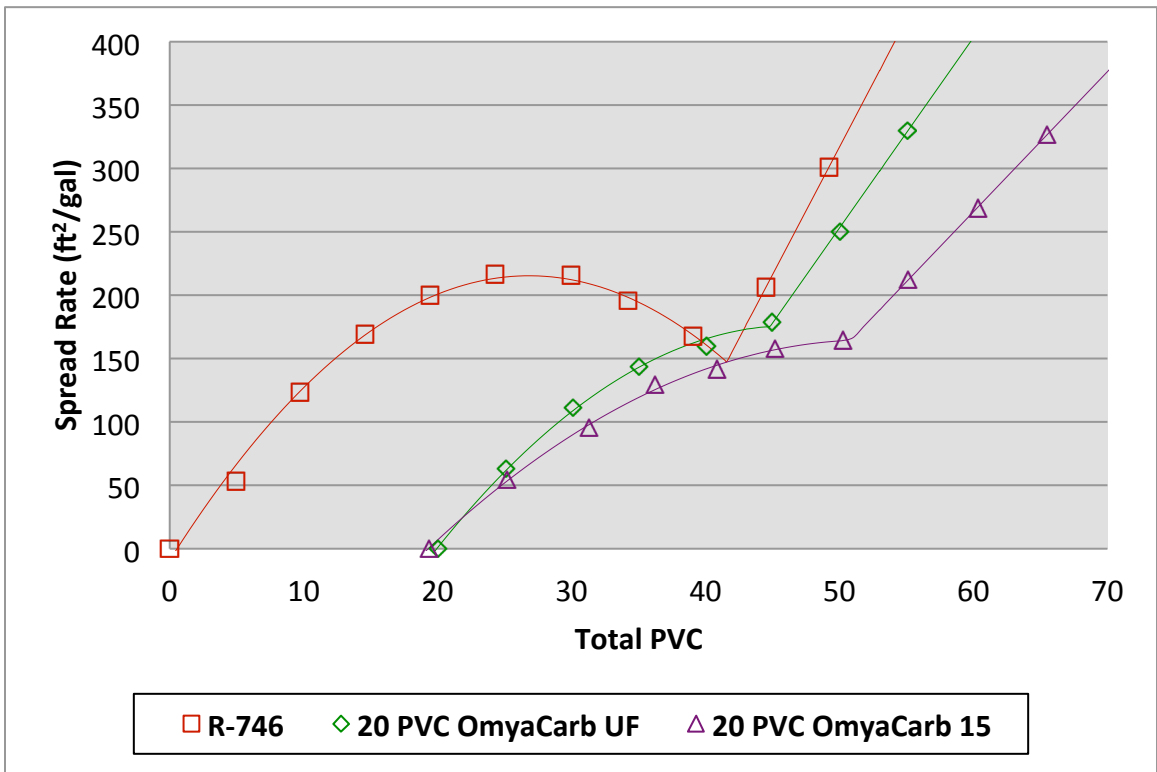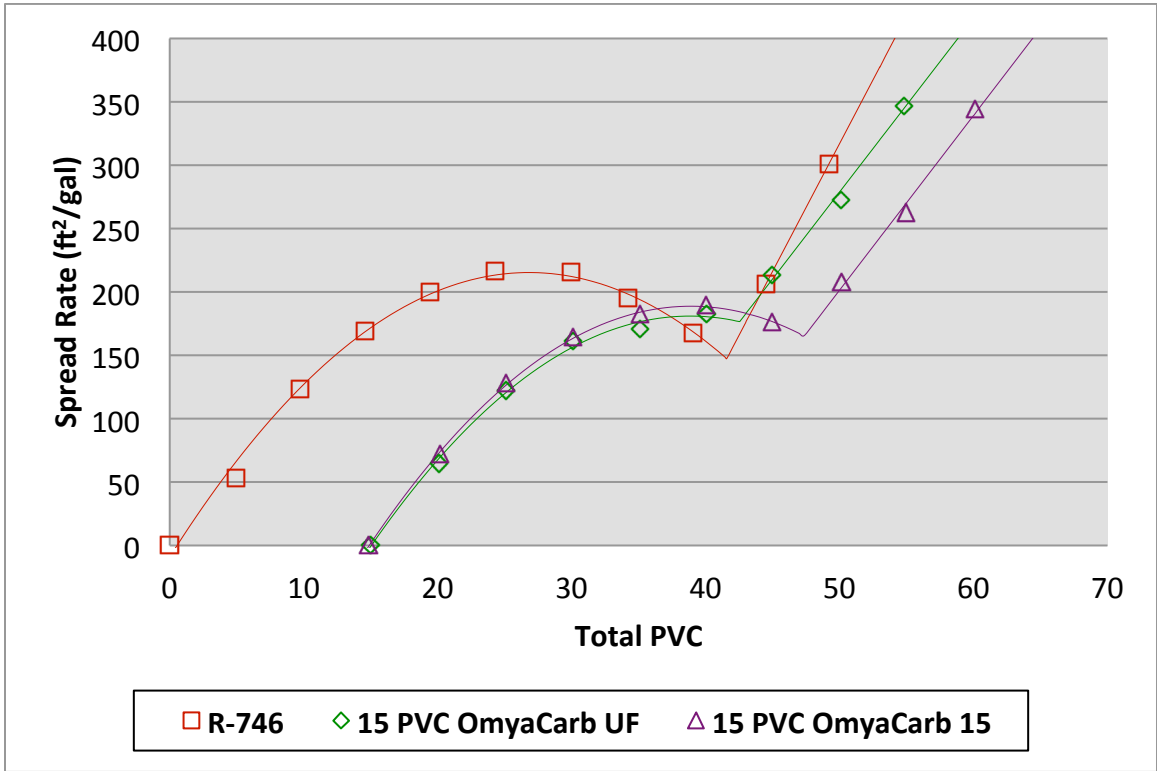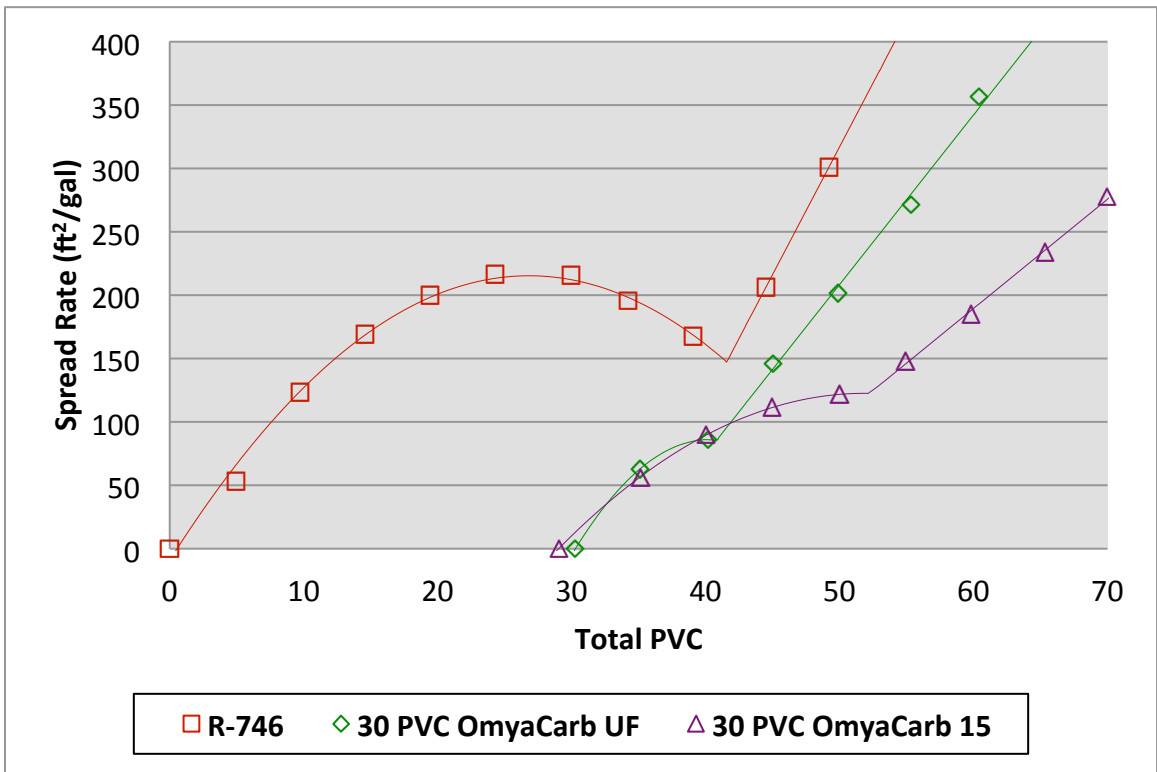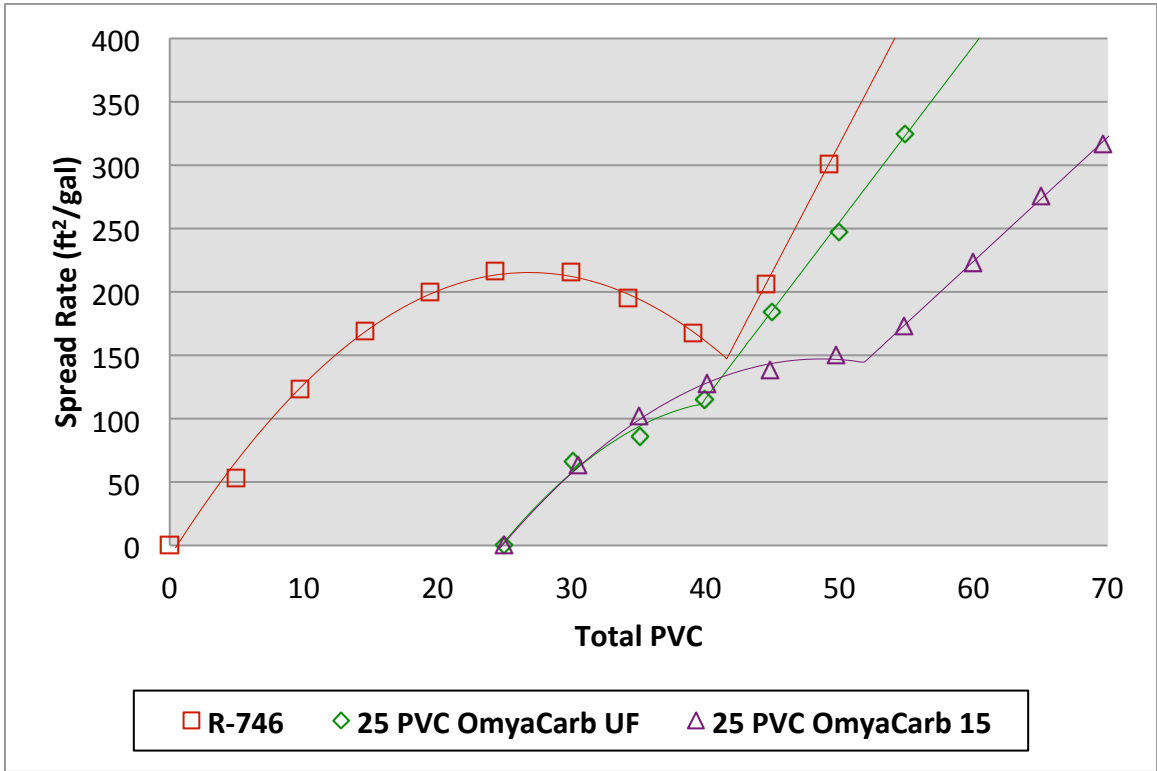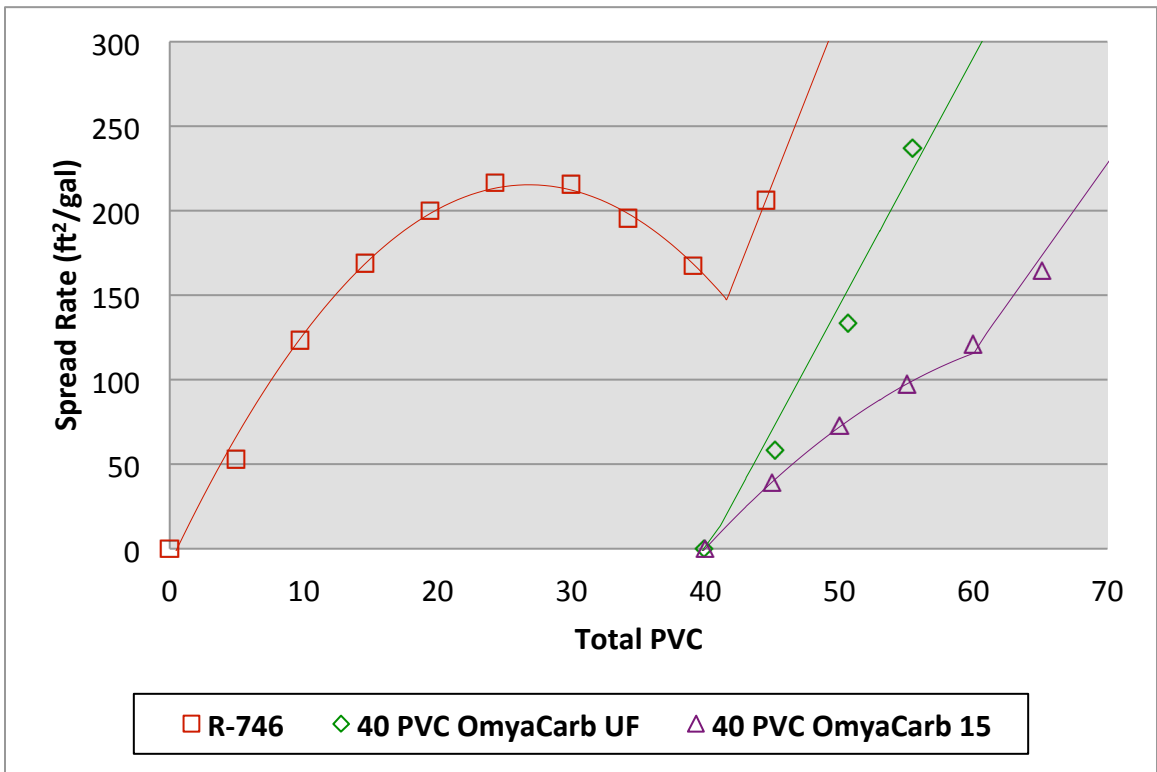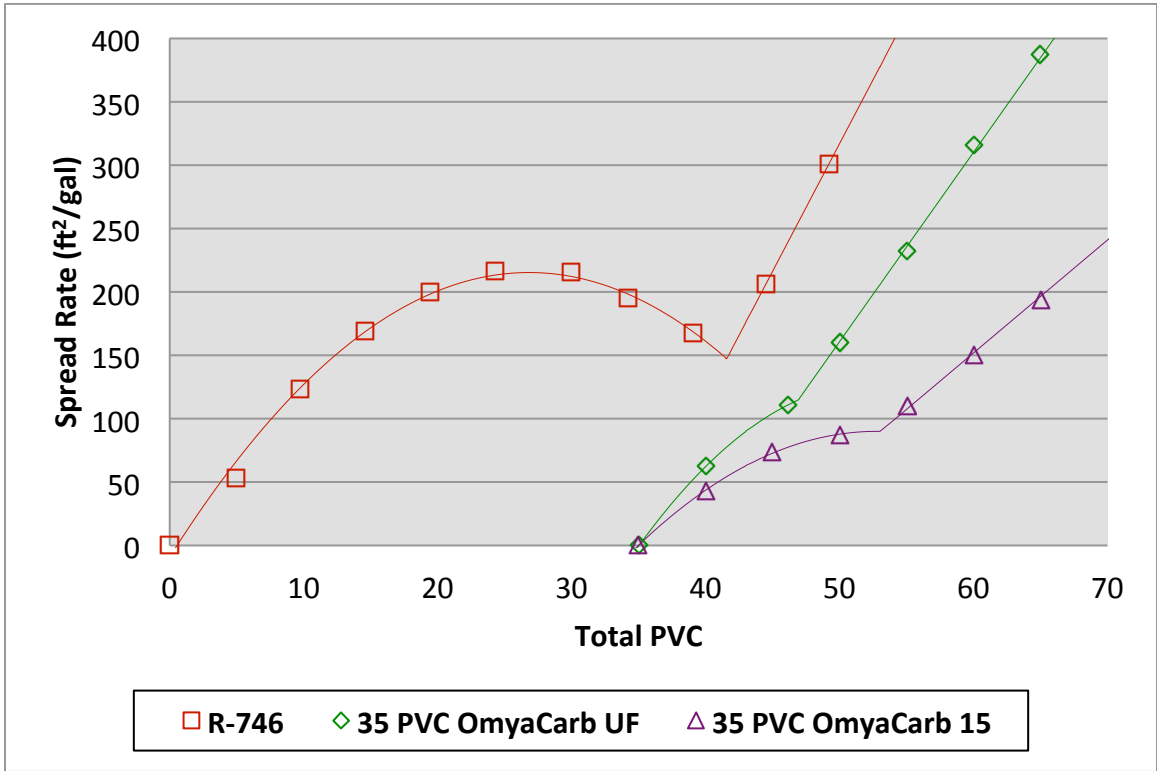
Appendix D: Paint Drawdown Raw Data – TiO₂ Only

TiO$_2$ PVC	Extender PVC	Resin	Paint Density [lbs/gal]	TiO$_2$ Content [lbs/gal]	R o White	R o Black	Weight [grams]	S Rate [ft^2/gal]
R-746								
0.00	0.00	100.00						0.00
4.95	0.00	95.05	8.81	0.38	0.88	0.72	4.00	53.08
9.72	0.00	90.28	9.10	0.72	0.90	0.82	4.16	123.57
14.60	0.00	85.40	9.40	1.11	0.90	0.82	3.28	169.19
19.44	0.00	80.56	9.64	1.47	0.91	0.84	3.40	200.11
24.30	0.00	75.70	9.89	1.84	0.92	0.86	3.52	216.59
29.93	0.00	70.07	10.15	2.28	0.92	0.87	3.67	215.56
34.19	0.00	65.81	10.32	2.58	0.93	0.87	3.75	195.59
39.05	0.00	60.95	10.52	2.94	0.93	0.87	3.81	167.59
44.50	0.00	55.50	10.72	3.37	0.94	0.90	3.88	206.18
49.22	0.00	50.78	10.90	3.70	0.95	0.91	3.93	301.34
R-741								
0.00	0.00	100.00						0.00
5.01	0.00	94.99	8.81	0.35	0.86	0.52	2.68	53.92
10.01	0.00	89.99	8.98	0.88	0.87	0.69	2.79	89.60
15.02	0.00	84.98	9.24	1.31	0.89	0.77	2.93	123.46
20.05	0.00	79.95	9.47	1.75	0.90	0.82	3.03	162.38
25.01	0.00	74.99	9.71	2.19	0.91	0.84	3.12	186.20
30.00	0.00	70.00	9.89	2.63	0.92	0.86	3.22	193.64
35.93	0.00	64.07	10.17	3.19	0.93	0.89	3.34	297.60
40.07	0.00	59.93	10.33	3.50	0.94	0.91	3.32	391.74
44.93	0.00	55.07	10.55	3.93	0.95	0.93	3.37	506.73
49.95	0.00	50.05	10.73	4.39	0.96	0.94	3.43	648.75

Appendix E: Paint Drawdown Raw Data – Omyacarb 15

TiO$_2$ PVC	Extender PVC	Resin	Paint Density [lbs/gal]	TiO$_2$ Content [lbs/gal]	R o White	R o Black	Weight [grams]	S Rate [ft^2/gal]
5% O15								
0.00	5.04	94.96						0.00
4.97	4.79	90.24	8.96	0.37	0.86	0.62	2.70	50.57
10.02	4.53	85.45	9.20	0.74	0.88	0.75	2.80	123.72
14.99	4.28	80.73	9.48	1.10	0.90	0.80	2.94	167.04
20.03	4.03	75.94	9.69	1.47	0.90	0.82	3.01	196.72
25.03	3.78	71.19	9.95	1.84	0.91	0.83	3.10	203.20
30.01	3.53	66.46	10.15	2.21	0.91	0.84	3.25	204.12
36.30	3.21	60.49	10.34	2.73	0.92	0.85	3.28	186.29
39.97	3.03	57.00	10.50	2.94	0.92	0.86	3.30	193.73
45.07	2.77	52.16	10.69	3.32	0.93	0.88	3.34	246.17
50.17	2.51	47.32	10.97	3.71	0.94	0.90	3.38	327.77
5PVC O15								
0.00	5.04	94.96						0.00
5.00	5.01	89.99	8.99	0.37	0.87	0.63	2.81	54.11
10.02	4.99	84.99	9.21	0.74	0.89	0.76	2.89	126.13
14.98	5.04	79.98	9.51	1.10	0.90	0.80	3.02	160.91
20.08	5.02	74.91	9.70	1.48	0.90	0.83	3.12	196.06
25.00	5.02	69.99	9.93	1.84	0.91	0.83	3.16	210.99
29.84	4.95	65.22	10.15	2.21	0.91	0.84	3.30	207.76
35.26	5.01	59.72	10.36	2.60	0.92	0.84	3.32	182.86
39.13	4.91	55.96	10.48	2.95	0.92	0.86	3.36	194.66
45.04	5.02	49.94	10.93	3.33	0.93	0.88	3.36	272.88
49.85	4.99	45.17	11.24	3.68	0.94	0.90	3.43	342.08
10% O15								
0.00	10.24	89.76						0.00
5.08	9.72	85.20	9.12	0.37	0.86	0.62	2.85	71.79
9.96	9.22	80.82	9.32	0.73	0.88	0.74	2.94	128.77
14.97	8.71	76.33	9.57	1.10	0.89	0.79	3.00	169.26
19.96	8.20	71.84	9.79	1.47	0.90	0.82	3.17	191.90

TiO$_2$ PVC	Extender PVC	Resin	Paint Density [lbs/gal]	TiO$_2$ Content [lbs/gal]	R o White	R o Black	Weight [grams]	S Rate [ft^2/gal]
25.10	7.67	67.23	10.10	1.85	0.90	0.83	3.26	209.68
30.06	7.16	62.78	10.26	2.21	0.91	0.84	3.31	203.71
35.26	6.63	58.11	10.36	2.60	0.91	0.84	3.28	176.22
39.96	6.15	53.89	10.68	2.96	0.92	0.86	3.26	213.53
45.01	5.63	49.36	10.86	3.32	0.93	0.88	3.29	256.24
10PVC O15								
0.00	10.24	89.76						0.00
4.98	10.25	84.76	9.13	0.37	0.86	0.62	2.80	55.03
9.97	10.24	79.78	9.39	0.74	0.88	0.75	2.97	125.78
15.06	10.27	74.67	9.68	1.11	0.89	0.79	3.13	166.97
20.00	10.35	69.65	9.84	1.48	0.90	0.81	3.17	181.88
25.15	10.25	64.61	10.01	1.86	0.90	0.82	3.27	188.88
29.92	10.25	59.83	10.23	2.21	0.91	0.83	3.35	180.51
35.91	10.08	54.01	10.42	2.69	0.91	0.84	3.32	184.85
39.87	10.24	49.89	10.73	2.94	0.92	0.86	3.41	235.91
15% O15								
0.00	14.85	85.15						0.00
5.00	14.10	80.89	9.23	0.37	0.86	0.61	2.88	60.68
10.01	13.36	76.63	9.46	0.74	0.88	0.73	2.92	120.93
15.03	12.61	72.36	9.65	1.11	0.89	0.79	3.08	162.19
20.00	11.88	68.12	9.85	1.47	0.89	0.81	3.17	182.37
24.99	11.14	63.87	10.11	1.84	0.90	0.82	3.24	195.50
30.21	10.36	59.43	10.34	2.24	0.90	0.83	3.29	195.40
34.95	9.66	55.40	10.48	2.58	0.91	0.83	3.29	193.73
39.82	8.93	51.25	10.61	2.94	0.92	0.86	3.26	243.38
15PVC O15								
0.00	14.85	85.15						0.00
5.07	15.14	79.79	9.25	0.37	0.85	0.62	2.90	72.12
9.97	15.14	74.88	9.52	0.74	0.87	0.73	2.99	128.32
15.04	15.08	69.87	9.74	1.11	0.88	0.78	3.12	164.15
19.83	15.28	64.89	9.96	1.47	0.89	0.80	3.21	182.29
24.99	15.03	59.98	10.20	1.84	0.89	0.81	3.21	189.76

TiO$_2$ PVC	Extender PVC	Resin	Paint Density [lbs/gal]	TiO$_2$ Content [lbs/gal]	R o White	R o Black	Weight [grams]	S Rate [ft^2/gal]
29.97	15.00	55.03	10.27	2.21	0.90	0.81	3.19	176.29
35.13	15.03	49.83	10.50	2.59	0.90	0.83	3.23	207.55
39.80	15.17	45.03	10.74	2.94	0.91	0.86	3.31	262.51
44.93	15.21	39.87	11.05	3.31	0.93	0.89	3.45	344.68
20% O15								
0.00	19.37	80.63						0.00
5.02	18.40	76.58	9.34	0.37	0.85	0.61	2.92	64.35
9.98	17.44	72.58	9.44	0.74	0.87	0.72	2.98	111.44
15.04	16.46	68.50	9.73	1.11	0.89	0.78	3.11	153.92
20.04	15.49	64.47	9.93	1.47	0.89	0.80	3.17	173.22
24.99	14.53	60.48	10.17	1.84	0.89	0.81	3.21	180.59
29.99	13.56	56.45	10.28	2.20	0.90	0.81	3.21	170.97
35.05	12.58	52.37	10.58	2.58	0.91	0.83	3.25	199.42
40.06	11.61	48.33	10.61	2.95	0.91	0.85	3.27	230.83
45.01	10.65	44.34	10.84	3.31	0.92	0.88	3.27	295.23
20 PVC O15								
0.00	19.37	80.63						0.00
5.03	20.12	74.85	9.35	0.37	0.86	0.61	3.00	54.80
9.87	21.46	68.67	9.61	0.74	0.87	0.71	3.16	95.79
14.69	21.55	63.76	9.91	1.11	0.88	0.76	3.28	129.38
19.80	21.07	59.14	9.97	1.49	0.89	0.78	3.28	141.27
24.73	20.47	54.80	10.21	1.84	0.89	0.79	3.29	157.79
29.88	20.38	49.74	10.33	2.21	0.89	0.80	3.26	164.55
34.92	20.20	44.88	10.61	2.58	0.90	0.83	3.35	212.31
40.09	20.23	39.68	10.93	2.95	0.91	0.86	3.45	268.92
44.79	20.69	34.53	11.31	3.34	0.92	0.88	3.64	326.72
25% O15								
0.00	24.96	75.04						0.00
5.39	23.61	70.99	9.50	0.40	0.85	0.61	3.06	65.22
10.26	22.40	67.34	9.66	0.75	0.87	0.73	3.16	113.20
15.17	21.17	63.65	9.87	1.12	0.88	0.77	3.22	142.80
20.64	19.81	59.55	10.06	1.53	0.89	0.78	3.28	157.85

TiO$_2$ PVC	Extender PVC	Resin	Paint Density [lbs/gal]	TiO$_2$ Content [lbs/gal]	R o White	R o Black	Weight [grams]	S Rate [ft^2/gal]
25.36	18.63	56.01	10.19	1.88	0.89	0.79	3.20	166.29
30.12	17.44	52.44	10.39	2.22	0.89	0.80	3.23	168.63
35.15	16.19	48.66	10.52	2.60	0.90	0.83	3.24	201.29
39.71	15.05	45.24	10.68	2.96	0.91	0.85	3.27	239.80
45.32	13.65	41.03	10.98	3.36	0.92	0.88	3.36	304.72
25 PVC O15								
0.00	24.96	75.04						0.00
5.78	24.70	69.52	9.53	0.43	0.86	0.63	3.23	63.18
10.13	24.92	64.95	9.71	0.75	0.87	0.72	3.33	102.34
15.26	24.86	59.87	9.90	1.13	0.88	0.76	3.31	127.64
19.91	24.90	55.19	10.00	1.48	0.88	0.77	3.28	138.25
25.01	24.76	50.23	10.44	1.86	0.89	0.78	3.30	149.84
29.87	24.94	45.19	10.54	2.20	0.89	0.80	3.34	173.37
35.25	24.76	39.99	10.83	2.62	0.90	0.84	3.46	223.24
40.11	24.92	34.97	11.09	2.96	0.91	0.86	3.63	276.03
44.80	24.82	30.38	11.50	3.33	0.92	0.88	3.76	316.81
30% O15								
0.00	29.02	70.98						0.00
5.19	27.51	67.30	9.56	0.38	0.85	0.58	2.80	59.77
9.97	26.12	63.90	9.74	0.74	0.87	0.69	2.86	100.62
15.08	24.64	60.28	9.90	1.11	0.88	0.73	2.90	126.96
20.20	23.15	56.64	10.07	1.49	0.88	0.75	2.89	140.78
25.21	21.70	53.09	10.16	1.86	0.89	0.79	3.23	148.20
29.99	20.32	49.70	10.31	2.21	0.90	0.79	3.34	137.22
35.29	18.78	45.93	10.36	2.61	0.90	0.82	3.34	174.41
39.83	17.46	42.71	10.52	2.95	0.91	0.85	3.40	219.51
30 PVC O15								
0.00	29.02	70.98						0.00
4.99	30.13	64.88	9.64	0.37	0.86	0.60	3.26	56.20
10.00	30.03	59.97	9.83	0.74	0.87	0.69	3.27	89.94
14.96	30.02	55.02	10.04	1.11	0.88	0.73	3.21	111.50
20.01	30.02	49.98	10.25	1.47	0.88	0.75	3.27	121.73

TiO$_2$ PVC	Extender PVC	Resin	Paint Density [lbs/gal]	TiO$_2$ Content [lbs/gal]	R o White	R o Black	Weight [grams]	S Rate [ft^2/gal]
24.95	29.98	45.08	10.37	1.84	0.89	0.77	3.35	148.10
29.90	29.91	40.19	10.65	2.21	0.90	0.81	3.35	185.10
34.63	30.70	34.66	10.81	2.57	0.91	0.84	3.52	234.01
39.93	30.06	30.00	11.38	2.95	0.92	0.87	3.79	277.72
35% O15								
0.00	34.96	65.04						0.00
5.01	33.21	61.78	9.59	0.37	0.85	0.59	2.69	74.30
10.02	31.45	58.53	9.78	0.74	0.87	0.69	2.79	108.07
15.03	29.70	55.27	9.88	1.11	0.88	0.73	2.93	129.67
20.71	27.72	51.57	10.51	1.54	0.88	0.76	3.33	128.60
24.89	26.25	48.85	10.21	1.87	0.89	0.78	3.12	154.15
30.11	24.43	45.46	10.34	1.35	0.89	0.80	3.22	186.46
34.98	22.73	42.29	10.59	2.58	0.91	0.85	3.34	242.36
39.97	20.99	39.05	10.88	2.96	0.92	0.88	3.32	320.55
35 PVC O15								
0.00	34.96	65.04						0.00
5.02	35.02	59.96	9.74	0.37	0.86	0.57	3.29	43.05
9.99	35.01	55.00	9.93	0.74	0.87	0.67	3.26	73.62
14.99	35.07	49.95	10.04	1.11	0.88	0.72	3.40	87.67
19.98	35.10	44.93	10.71	1.48	0.88	0.74	3.56	110.44
24.96	35.07	39.97	10.93	1.85	0.89	0.79	3.62	150.28
29.95	35.11	34.94	11.29	2.21	0.90	0.82	3.67	193.55
35.04	35.05	29.92	11.34	2.59	0.91	0.85	3.71	244.69
40% O15								
0.00	39.95	60.05	9.74	0.00	0.82	0.07	3.21	0.00
5.03	37.94	57.03	9.74	0.37	0.85	0.54	3.21	34.46
10.06	35.93	54.01	9.93	0.74	0.86	0.65	3.18	70.54
15.02	33.95	51.03	10.04	1.10	0.87	0.69	3.21	87.90
20.02	31.95	48.03	10.71	1.47	0.88	0.73	3.19	118.99
25.03	29.95	45.02	10.93	1.84	0.89	0.78	3.34	156.46
29.93	27.99	42.08	11.29	2.21	0.89	0.81	3.37	201.29
35.20	25.88	38.91	11.34	2.60	0.91	0.84	3.49	251.96

TiO$_2$ PVC	Extender PVC	Resin	Paint Density [lbs/gal]	TiO$_2$ Content [lbs/gal]	R o White	R o Black	Weight [grams]	S Rate [ft^2/gal]
40PVC O15								
0.00	39.95	60.05						0.00
5.00	40.00	55.00	9.91	0.37	0.85	0.55	3.14	38.94
9.99	40.01	50.00	10.11	0.74	0.86	0.65	3.23	72.83
15.00	40.04	44.97	10.24	1.10	0.87	0.70	3.24	97.30
19.96	40.02	40.02	10.56	1.47	0.88	0.74	3.39	120.82
25.27	39.82	34.91	10.95	1.87	0.89	0.79	3.56	164.41
29.88	40.24	29.88	11.15	2.21	0.90	0.84	3.78	233.88

Appendix F: Paint Drawdown Raw Data – Omyacarb UF

TiO$_2$ PVC	Extender PVC	Resin	Paint Density [lbs/gal]	TiO$_2$ Content [lbs/gal]	R o White	R o Black	Weight [grams]	S Rate [ft^2/gal]
5 PVC OUF								
0.00	5.08	94.92	8.73	0.00	0.82	0.02	2.53	0.00
5.07	5.13	89.81	8.95	0.37	0.85	0.62	2.64	73.28
10.18	5.00	84.83	9.24	0.75	0.88	0.74	2.71	141.61
15.01	5.51	79.48	9.43	1.11	0.89	0.79	2.84	185.44
20.05	4.98	74.97	9.70	1.48	0.90	0.82	2.96	215.56
24.77	5.91	69.32	9.83	1.83	0.91	0.84	3.05	207.23
29.97	5.11	64.92	10.14	2.21	0.92	0.85	3.16	205.87
34.80	5.09	60.12	10.37	2.57	0.92	0.85	3.18	172.34
39.89	5.20	54.92	10.53	2.95	0.92	0.87	3.20	221.18
44.86	5.16	49.98	10.59	3.31	0.93	0.89	3.21	289.56
49.98	5.10	44.92	10.78	3.69	0.94	0.91	3.24	382.19
10 PVC OUF								
0.00	10.34	89.66	8.86	0.00	0.82	0.03	2.55	0.00
5.04	10.05	84.91	9.09	0.37	0.85	0.62	2.67	69.36
10.04	10.05	79.91	9.38	0.74	0.88	0.74	2.81	129.75
15.04	10.10	74.86	9.55	1.11	0.89	0.80	2.93	168.98
20.01	10.08	69.91	9.76	1.48	0.90	0.82	3.02	186.29
24.95	10.14	64.91	9.96	1.84	0.91	0.84	3.13	181.56
29.96	10.11	59.94	10.16	2.21	0.92	0.85	3.17	164.68
34.81	10.12	55.07	10.41	2.57	0.92	0.86	3.13	200.11
39.99	10.16	49.85	10.55	2.95	0.93	0.88	3.14	295.23
44.89	10.16	44.95	10.73	3.32	0.95	0.92	3.31	473.19
49.29	10.46	40.24	11.11	3.64	0.95	0.93	3.46	563.50
15 PVC OUF								
0.00	14.96	85.04	8.99	0.00	0.82	0.04	2.74	0.00
5.00	15.12	79.88	9.24	0.37	0.85	0.61	2.80	64.80
9.98	15.11	74.91	9.46	0.74	0.88	0.74	2.91	122.38
14.98	15.09	69.93	9.73	1.10	0.89	0.79	3.05	161.03
20.05	15.06	64.89	9.82	1.47	0.90	0.82	3.11	170.97

TiO$_2$ PVC	Extender PVC	Resin	Paint Density [lbs/gal]	TiO$_2$ Content [lbs/gal]	R o White	R o Black	Weight [grams]	S Rate [ft^2/gal]
25.01	15.03	59.96	10.10	1.84	0.91	0.83	3.16	182.37
29.93	15.00	55.07	10.32	2.20	0.91	0.85	3.14	213.42
34.98	15.11	49.92	10.43	2.57	0.92	0.87	3.16	272.70
39.84	14.99	45.17	10.60	2.93	0.93	0.89	3.21	347.03
44.62	15.20	40.18	10.88	3.28	0.94	0.91	3.26	414.88
20 PVC OUF								
0.00	20.06	79.94	9.21	0.00	0.82	0.04	2.78	0.00
5.02	20.09	74.89	9.35	0.37	0.86	0.62	2.88	63.13
10.00	20.06	69.94	9.56	0.74	0.88	0.74	2.97	111.35
14.98	20.01	65.00	9.83	1.10	0.89	0.79	3.06	143.56
20.00	20.08	59.92	10.02	1.47	0.90	0.81	3.10	159.52
24.95	20.02	55.03	10.11	1.83	0.91	0.83	3.06	179.00
29.95	20.10	49.95	10.36	2.20	0.92	0.86	3.07	250.25
34.90	20.15	44.95	10.68	2.56	0.93	0.89	3.10	329.89
39.88	20.15	39.97	11.14	2.93	0.93	0.90	3.15	412.78
45.50	19.70	34.80	11.40	3.34	0.94	0.91	3.22	475.40
25 PVC OUF								
0.00	24.96	75.04	9.32	0.00	0.82	0.06	2.84	0.00
5.02	25.08	69.90	9.48	0.37	0.86	0.61	2.91	66.27
9.97	25.12	64.91	9.67	0.73	0.88	0.72	3.00	85.72
14.98	24.95	60.07	9.87	1.10	0.89	0.77	3.01	115.12
20.07	24.92	55.00	10.14	1.47	0.90	0.82	3.02	184.02
24.93	25.01	50.06	10.20	1.83	0.91	0.86	3.02	247.52
29.91	24.96	45.12	10.42	2.20	0.93	0.88	3.10	324.63
34.96	25.34	39.70	10.92	2.57	0.93	0.90	3.17	410.70
40.04	25.14	34.82	11.26	2.94	0.94	0.91	3.18	473.19
45.61	24.65	29.74	11.54	3.35	0.94	0.92	3.29	525.02
30 PVC OUF								
0.00	30.29	69.71	9.39	0.00	0.82	0.08	2.97	0.00
5.00	30.09	64.91	9.62	0.37	0.86	0.62	3.05	62.80
10.00	30.16	59.85	9.84	0.74	0.88	0.72	2.98	86.12
14.99	30.03	54.98	10.05	1.11	0.89	0.79	3.01	145.87

TiO$_2$ PVC	Extender PVC	Resin	Paint Density [lbs/gal]	TiO$_2$ Content [lbs/gal]	R o White	R o Black	Weight [grams]	S Rate [ft^2/gal]
19.84	30.01	50.15	10.27	1.47	0.91	0.83	3.04	201.49
24.59	30.78	44.63	10.48	1.82	0.92	0.87	3.10	271.43
29.88	30.56	39.57	10.77	2.21	0.93	0.89	3.15	356.44
34.83	30.04	35.13	10.97	2.58	0.94	0.91	3.27	417.86
39.30	29.85	30.85	11.26	2.91	0.94	0.91	3.32	455.72
35 PVC OUF								
0.00	35.04	64.96	9.49	0.00	0.82	0.08	3.01	0.00
5.06	34.98	59.96	9.54	0.36	0.86	0.61	2.99	62.60
11.92	34.23	53.86	9.82	0.86	0.89	0.76	3.02	110.89
15.03	35.00	49.97	9.95	1.08	0.90	0.81	3.03	160.27
19.95	35.05	45.00	10.05	1.43	0.91	0.85	3.09	232.41
25.00	35.03	39.97	10.27	1.80	0.92	0.88	3.18	315.58
29.91	35.04	35.05	10.75	2.15	0.93	0.90	3.26	387.28
34.90	35.02	30.09	11.05	2.51	0.94	0.91	3.42	454.20
40 PVC OUF								
0.00	39.86	60.14	9.59	0.00	0.82	0.11	2.96	0.00
5.02	40.18	54.80	9.67	0.36	0.86	0.62	2.95	58.37
10.35	40.29	49.36	9.80	0.74	0.88	0.77	2.95	133.27
15.54	39.90	44.56	10.32	1.12	0.91	0.84	3.07	237.28
21.25	39.25	39.50	10.57	1.53	0.92	0.88	3.12	319.79
24.85	39.95	35.20	10.66	1.78	0.93	0.89	3.15	359.91
29.95	39.98	30.08	11.04	2.15	0.93	0.90	3.23	423.07