A Novel Silica-Based Nano Pigment as a Titanium Dioxide Replacement

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A NOVEL SILICA-BASED NANO PIGMENT AS A TITANIUM DIOXIDE REPLACEMENT

by

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A thesis submitted to the Graduate College in partial fulfillment of the requirements for the degree of Master of Science in Paper and Imaging Science and Engineering Western Michigan University
June 2014

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A NOVEL SILICA-BASED NANO PIGMENT AS A TITANIUM DIOXIDE REPLACEMENT

Ryan Stoneburner, M.S.
Western Michigan University, 2014

This research focused on the evaluation of a new Silica-based pigment for the replacement of titanium dioxide (TiO$_2$) in paperboard coatings. The silica-based pigment has shown the ability to be a replacement in terms of functionality and runnability. TiO$_2$ is currently the highest opacifying pigment used in paper coatings, but it is also the most costly. Finding a less expensive pigment that doesn't reduce effectiveness is critical to reducing the cost of TiO$_2$ formulations.

To evaluate the new pigment, coatings will be applied using a Cylindrical Laboratory Coater (CLC) with varying amounts of TiO$_2$ and silicate nanofibers to a paperboard substrate. Tests including appearance, mottle, smoothness, gloss and other physical properties will be tested to see if they are affected upon replacement of TiO$_2$.

Upon evaluation of the results, at low to medium replacements of TiO$_2$ with silicate nanofiber particles, there was little effect on most of the properties tested. This indicates that it is feasible to replace the TiO$_2$, since the quality of the coated paperboard wouldn't be significantly reduced. Therefore, the cost savings associated with replacing the more expensive TiO$_2$ pigment with a pigment that is 1/8 the cost would be financially beneficial.
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INTRODUCTION

Over the years, alternatives for natural pigments have been sought. The ability to synthetically create pigments suitable for coatings would be beneficial due to the ability to tightly control and optimize their properties. Currently, pigments are mined, processed, in some cases modified, and then sold to various paint and coating companies. Being able to synthetically produce pigments would help to curb shortages on certain pigments, reduce costs, and save time and energy.

It is inevitable that the market trends for the paper industry will continue to significantly change. Due to electronic media, paper producers have had to increase the quality of their products to be able to compete for customers. This has caused an increase in competition between paper companies and in turn, increased the demand for quality at a decreased cost. One of the areas that has seen the biggest increase in competition has been in paperboard in the form of product displays and packaging. This is due to a demand for better print quality, where as in the past, these grades weren't printed as much or had lower standards. This means that printed paperboard is now competing in markets where it did not compete before.

Coated paperboard currently accounts for about 6 million tons/year and is increasing compared to coated paper grades which account for 7.5 million tons/yr but are decreasing[1, 2]. The demand for coated paper will most likely continue to decrease, as it has for the past 7 years, as the markets for coated paper products decrease, i.e. magazines, catalogs, and photographs[1]. Even with the newer
demand for coated paperboard, uncoated paperboard products still outweigh the production of coated paperboard products. This leaves an encouraging potential for an increase in the future production of coated paperboard as technologies improve and the gap in production between coated paperboard and other markets decrease.

**Coatings**

Paper coatings at their most basic definition help to improve certain desired qualities that the substrate doesn't provide. These qualities could be roughness, opacity, surface quality, functionality, and improved print properties. A coating is defined as a material which is applied onto a surface and appears as either a continuous or discontinuous film after drying[3]. It is first applied to a substrate, metered, dried, and then smoothed. Coatings are designed to be able to flow in between the voids of the fibers in the substrate, which results in a more uniform layer. The deviations between the pigment particles are much less than the deviations between fibers, which increases the smoothness of the sheet.

Coatings that are applied to paper substrates can be separated into two broad categories: pigmented coatings and functional coatings. Functional coatings add a unique property besides the classical properties of a coating (i.e. smoothness and opacity). The unique properties that can be added to these types of coatings can be, but are not limited to: friction control, release properties, abrasion resistance, barrier properties (grease, oil, water, vapor), and certain printing characteristics.
The structure system of a coating can be thought of in four regions: substrate, film, substrate/film interface, and film/air interface. Understanding how all of the regions or layers interact and work together are key to creating an ideal product. Table 1 shows the importance of each layer and how it affects the rest of the system. Since each layer of a coating system builds upon each other, having a suitable substrate is very important. The quality of the paper substrate has a direct effect on the appearance of the coating. If the base sheet is too open (too many voids between the fibers) or closed, or the uniformity is bad, the finished coated product will show signs of this. For instance, the coating film could be uneven, resulting in high roughness or the coating could look non-uniform, which would cause poor print quality.

Table 1. Importance of Layers in Coating System[3]

<table>
<thead>
<tr>
<th>Region</th>
<th>Properties/Importance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film/Air Interface</td>
<td>Light Reflection (Gloss) Friction Control Surface Hardness Surface Porosity Surface Energy</td>
</tr>
<tr>
<td>Film</td>
<td>Opacity Color Water/Solvent Uptake Barrier Properties</td>
</tr>
<tr>
<td>Substrate/Film Interface</td>
<td>Adhesion Durability</td>
</tr>
<tr>
<td>Substrate</td>
<td>Surface Quality Sheet Porosity</td>
</tr>
</tbody>
</table>

A coating is made up of several ingredients that work together to provide the desired enhancements. A coating can consist of pigments, binders, and additives. Depending on what is required of the coating, the ratios and
combinations of these ingredients will vary. Table 2 shows examples of various coating ingredients and why they are used.

Table 2. Ingredient Functionality in a Coating

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pigments</strong></td>
<td></td>
</tr>
</tbody>
</table>
| Clay, Calcium Carbonate, TiO₂, Talc | -Provides the foundation of the coating  
-Impact brightness and smoothness  
-Impacted by substrate being used |
| **Binders**           |                                                                           |
| Starch, Latex, Protein | -Binds the pigments together  
-Can increase viscosity of coating |
| **Lubricants**        |                                                                           |
|                        | -Allows particles within the coating to slide past one another which can achieve higher solids and better gloss |
| **Rheology Modifiers**|                                                                           |
|                        | -Adjusts the viscosity and water retention of the coating to maximize runnability |
| **Brightening Agents**|                                                                           |
|                        | -Adds brightness to the coating when pigments don't suffice              |
| **Defoamers**         |                                                                           |
|                        | -Decreases accumulation of foam during application                       |
| **Crosslinkers**      |                                                                           |
|                        | -Chemically bonds the binders for added strength and durability           |

Along with all of the benefits of using coatings, cost is another very important reason coatings are used. Pigments that are used in coatings are less expensive than using fibers. This results in a more cost effective product by maintaining a grade weight but using less paper fibers. The coating can account for up to 5-20% of the weight of a coated paperboard grade. By using coatings,
not only can the quality of the surface and functionality of the paper increase, but the cost of production of a specific grade is decreased.

Coatings can be applied to a substrate through many techniques, all of which have unique benefits. The coating methods used are dictated by the speed of the machine, substrate type, and the desired quality of the coating. Coated paper mills may need the coating embedded into the paper. This is accomplished by using a size press coater. The need for a coating of uniform thickness and high coverage is best achieved with an air knife or curtain coater. A very smooth coating surface is best achieved with a blade coater. All of these methods also have disadvantages as well, as in decreased sheet strength, rougher surfaces, and non-uniform coating thickness, respectively. For coated paperboard, an air knife or curtain coater is often used to meter the applied top coating layer.

Using a metering technique that applies a uniform coating layer is very critical when coating paperboard. The color of the darker substrate and higher surface roughness present in these grades must be taken into account. Ideally, the mill would like to have the smoothest sheet possible. The balance between increasing the smoothness to help increase print quality and low mottle and high stiffness is difficult. Blade metering provides high smoothness, but results in a coating layer of varying thickness. This is because it meters more coating into the valleys of a rough surface and less coating onto its peaks. So in the case where the substrate is much darker than the coating, mottle occurs. Therefore, for these applications, metering techniques are used where a coating layer of uniform thickness is achieved. This helps to provide a coating layer that makes the darker
surface more uniformly bright. However, the drawback is that the coating won't be as smooth, even upon calendering.

**Paperboard Substrates**

Paperboard is distinguished from paper by its higher basis weight, which can range between 150-800 g/m². Paperboard may be made out of one or multiple layers of paper which may also contain recycled fibers. The layers are bonded together either by fiber-to-fiber bonding or adhesives.

Paperboard has a relatively high absolute strength in comparison to other papers, but is produced at slower rates. Due to the lower speeds of production and the higher comparative basis weights, machine sheet breaks don't happen frequently. This results in a high uptime for the machine and therefore the coating is done on-line instead of offline. Also, by coating on-line, the curl of the paperboard can be controlled[4].

The formulation of a top-coating formulation for paperboard depends greatly on the nature of the substrate. Paperboard is pre-coated to reduce consumption of the more expensive top coating. A pre-coat is applied as a cheaper alternative to achieve the quality desired from the finished product while reducing cost. To do this, pre-coatings are made with less expensive pigments and usually less expensive ingredients.
Calendering

Calendering is a mechanical action used to modify coated and uncoated paper and is most often used to increase the gloss and smoothness of a sheet. Other properties such as density, blackening, brightness, and opacity are also affected. Calendering is a process of running paper through a nip point where two rolls meet under pressure to flatten the paper and coating. This flattening process is designed to also align the fibers and the pigment particles, which causes a smoother surface. Nip pressure, dwell time, roll elasticity, roll temperature and smoothness are all factors that influence the results. Increasing the nip pressure and roll hardness will decrease the caliper, lowering stiffness, while increasing temperature may allow for the particles in the paper and coating to move a little easier, thus being able to decrease the load pressure to achieve smoothness with less loss in caliper[5].

Pigments

The demands for runnability and optical property performance for all coating pigments is constantly increasing. Thus, the pigment properties of particle size, impurities, surface shape, and surface area are increasingly more important. These factors help to determine the packing arrangement of the pigment particle and pigment particle interactions. The way in which the particles pack in the dry coating layer determines all of the properties attributed to the finished product. One author has described what the factors affecting particle packing as the "Seven S factors": size, shape, surface, spacing (geometric),
structure, spread (size distribution), and stirring[6]. Knowing and understanding these factors, the properties desired from an ideal pigment would be:

- appropriate particle size and narrow particle distribution
- free from impurities
- good dispersibility for easy mixing with water and low water absorption
- high chemical stability and low solubility in water
- good compatibility with other coating components
- good light reflectivity at all wavelengths for high brightness
- high refractive index for good opacity
- good glossing properties for eye-pleasing coating gloss and high print gloss
- low binder demand
- good flow properties in an aqueous suspension and low abrasiveness
- cheapness[7]

Because any one pigment does not offer all of these desired properties mixtures of different pigments (i.e. Clays, Calcium Carbonates, Titanium Dioxide and Talc) are used to combine their strengths to include as many of the properties listed above.

Since a coating formulation may be adjusted by changing the ratios of the pigments used, understanding the weight-versus-volume substitutions of pigments is very important in terms of binder demand and optical property performance. Binder demand can be understood as the amount of binder necessary to fully fill the voids in between all of the pigment particles in the system. The term invented in the mid-1950's by the paint industry, Critical Pigment Volume Concentration (CPVC), describes how much binder is needed to eliminate the air voids between pigments. A PVC of 100% is understood to be all pigment while a PVC of 0% is all binder. These extreme PVC values are not ideal because a coating containing both binder and pigment is desired. These values do however help describe where the CPVC value lies. A PVC value above the CPVC value means air voids are
created due to a lack of binder and a PVC below the CPVC value means the pigments start to lose contact with one another due to too much binder[6].

As the PVC increases, the air voids increase and the binder in the coating decreases. The binder acts like a glue to hold the pigment particles together. As the ratio of the binder and pigment changes, the gloss of the coating is the most noticeable property to change. As there is less binder in the coating, the air voids become more prominent, which increases the porosity of the coating. This also increases the opacity of the coating as air has a lower refractive index than binder. The corrosion resistance decreases as the amount of binder in the system decreases because the strength of the coating decreases. It should be noted that all paperboard coatings are made above the CPVC value to ensure air voids are present. Properties such as porosity, gloss, and blister resistance can be altered in other ways than PVC, such as calendering.

Dispensing

In order to maximize the effects of the pigments used in the coatings, the pigments must be in a stable dispersed suspension. To disperse the pigment particles means to break apart each particle into the smallest form possible. Pigments like to clump together when allowed to sit over time and eventually settle out of suspension. High-speed dispersing refers to a saw-blade-type impeller mounted on a shaft rotating at high speed, which is vertically centered in an upright cylindrical tank[8]. This impeller works to apply mechanical energy to
the clumps of particles to break them apart to create a suspension of pigment particles.

A well dispersed pigment is always sought after to minimize coating viscosity, optimize surface area, and increase the optical properties. Pigments are completely dispersed when the particles are completely wetted. This means that the particles are completely separated and the viscosity of the pigment will no longer drop with the addition of more dispersing agent. A peripheral velocity of the impeller must reach about 4,900 rpm or higher for the good dispersion of a pigment for roughly 15-20 minutes under ideal conditions[8].

There are three forces to consider when creating any suspension: Electromagnetic, Electrostatic, and Steric Hindrance[6]. Dispersing agents are added to control the interactions of these forces to achieve the highest solids for the coating while maintaining a stable suspension. Higher solids are desirable because they help create a more uniform binder distribution due to reduced migration into the base paper, achieve a faster immobilization by containing less water, and generate significant savings in the dryer energy required[9].

Electromagnetic forces are attractive in nature and must be overcome to ensure flocculation of particles is prevented. As flocculation of particles occurs, the suspension loses stability and the runnability of the coating on the machine is negatively affected. The electromagnetic forces can be attributed to Van der Waals forces which are caused by interactions of the dipoles within the particles acting on one another.
Electrostatic forces are caused by like charges repelling each other. For instance, two negatively charged particles will repel each other. The repulsion caused by the electrostatic forces increases the stability of the suspension by increasing the distance between particles. This is caused by an unequal distribution of ions in the solution around the particle and at its surface. This implies a coating must have excess ions in the solutions and by increasing or decreasing the pH of the solution, particle interactions can be controlled.

The addition of an electrolyte into the slurry during dispersing is also needed to control electrostatic forces. These electrolytes are commonly referred to as dispersing agents. They work by attaching themselves to the generally negatively charged particles and in doing so can make the particle nonpolar. By creating a nonpolar shell around the particle, usually of only one molecule thick, the effective diameter is reduced. This is achieved by replacing several layers of water molecules that were present before the electrolyte was added. Now, the particles are less inclined to see each other and therefore decrease the viscosity of the slurry. This is an important role as the amount of solids achievable for any given slurry can now be increased. The higher the solids that a slurry of pigment can be made, the more cost efficient the coating process will be.

Steric hindrance is also helpful in creating a stable coating suspension, especially when used in combination with electrostatic forces. Steric hindrance is caused when materials are adsorbed on the surface of a particle. The adsorbed layer acts as a mechanical barrier between approaching particles. Materials such as proteins, gums, starches, and cellulosic derivatives work well. These
protective colloids are especially effective because they are strongly hydrophilic, giving them the ability to hold the water around them, creating even more steric hindrance.

**Opacity**

Opacity can be defined as the ratio of light being reflected off a black backing to the reflectance of light off a white backing. It is impacted by the refractive indexes of the particles and air voids in the system. The refractive index of a material is equivalent to the velocity of light in a vacuum divided by the velocity of light in a given medium. The greater the differences in R.I. between coating components, the higher the opacity will be. Thus, maximizing these differences results in higher hiding power. Light that reflects off the surface of the coating at the same angle of incidence is called specular reflectance, also known as the gloss of the surface. Light can also reflect at different angles depending on its contact with the particles in the coating system. This is known as diffuse reflectance. Light that passes through the solid interfaces is considered as diffuse transmittance. Minimizing the amount of light that can pass through the coating and paper board layers increases the opacity.

Air is used as the standard when rating refractive indices of pigments and has a R.I. of 1. Depending on the type of pigment used, the R.I. will be different. When comparing the refractive indices of TiO₂, anatase has a R.I. of 2.56 and rutile has a R.I. of 2.71. Comparing these refractive indices to the refractive indices of fibers and other pigments (Talc, CaCO₃, and Clay), they all fall within
a small R.I. range of roughly 1.55-1.65. Water has a refractive index of 1.33 which explains why substrates and coatings lose opacity when water replaces the air voids within these structures.

The light scattering ability of pigments in coatings is determined by the difference in refractive indices. By subtracting the known R.I.'s between a particle and the fluid it is encompassed by, the amount of light scattering can be understood. As the opacity of a coating increases, the light scattering increases as well. Maximizing the opacity of a coating is achieved by passing light through TiO$_2$ and air voids as these are the coating components greatest difference in R.I.

**Titanium Dioxide**

In comparison to the other coating pigments, TiO$_2$ is very expensive. For this reason it is used only in cases where coating opacity cannot be economically achieved by any other means. Generally, with higher basis weight paper grades, such as bleached paperboard, TiO$_2$ is not needed because sheet opacity is naturally obtained by the higher basis weight of the board. However, for darker paperboard grades such as recycled paperboard and unbleached Kraft grades, TiO$_2$ is used to obtain the needed coating opacity to hide the darker basesheet. TiO$_2$ also has an added benefit of offering superior brightness, which also increases the quality of the finished product in terms of appearance. The abrasive nature of this compound does offer a problem to printers, especially gravure printers, because of its abraisitivity, which wears down the engraved imaged cylinder and ink-metering doctor blade.
TiO₂, when used, will never be the most abundant pigment in a coating due to its high expense. The major pigments used are calcium carbonate and clay. Depending on the needs of the coating, TiO₂ is added to these pigments at smaller percentages when an increase in opacity is needed.

Major sources of TiO₂ are most readily exported from Australia, USA, India, and South Africa[10]. TiO₂ has three common crystalline poly forms: Anatase, Brookite, and Rutile. The anatase and rutile forms are the only ones used in paper coatings. The basic shape of the octahedral configuration remains constant between the two forms used, but they vary in the number of bonds they contain between each crystalline structure. The rutile phase has fewer bonds between each octahedral which allows for a less compact structure. This imparts more air voids within the TiO₂ crystals causing an increase in the opacity and consequently creating the desirability of the rutile form in paper coatings.

Several strategies have been attempted to create TiO₂ in a controlled environment. These methods include the vapor-phase method[11], combustion synthesis[12], hydrothermal[13, 14], sol-gel[15], microwave irradiation[16], and the hydrolysis and polycondensation of titanium alkoxides[17]. However, for the most effective light scattering, TiO₂ (anatase and rutile) should be a submicron, crystalline, spherical, and non-porous particle. Most methods above create a particle size that is acceptable with a narrow particle size distribution but can lack in the shape and porosity of the particle. The ideal particle size for TiO₂ is between 200-450 nm for the most effective light scattering. This is because the most effective particle size for scattering light is half the wavelength of visible
light, 400-700 nm. The flame-heating and alkoxide hydrolysis methods create spherical particles that are amorphous. Whereas the sulfate and chlorine processes don't make a spherical TiO$_2$ particle.

**CONCEPTS FOR TiO$_2$ REPLACEMENT**

Since the cost of TiO$_2$ is very expensive compared to other pigments, other sources of light scattering and high opacifying nanoparticles are constantly being pursued. For instance, finer GCC and calcined clays would increase the R.I. values from 1.6, by increasing the number of times light would have to pass through different mediums. There are also new developments in this area that include nanoparticle-coated pigments, transformations of deinking residuals (DIR), hollow sphere synthetic pigments, and silicate nanofibers. While the refractive indices and brightness values of these materials do not match that of TiO$_2$, they can increase opacity more than unmodified pigments.

Pigments such as calcined clay and GCC, while not having equal light scattering to TiO$_2$, are viable ways in which light can be scattered and absorbed at a lower cost. Advances in achieving smaller particle size is a way in which the light scattering can be increased. Results of increased light scattering and opacity from these pigments can be seen in a study looking at increasing opacity with fillers in a printing paper.

Light absorption ($K$) and scattering ($S$) properties of pigments, found from the Kubelka-Munk theory, can be compared to determine the most efficient pigments to use for opacity. The results from studies have shown both GCC and
calcined clay provide more opacity than using no pigment at all. Furthermore, this study showed that calcined clay is a better opacifying pigment than GCC or other types of clays. The loss of bonded water during the calcination process creates air voids between the thermally fused particles, which creates a greater surface area for light scattering[18].

A relatively new idea is the development of nanoparticle-coated pigments. These particles work to increase the efficiency of light scattering. The developers of the particles manipulated the size, shape, packing density, and refractive index of various particles to optimize opacity[19].

Studies performed with nanoparticle-coated pigment used a precipitated calcium carbonate (PCC) backbone with smaller pigments attached around it. PCC was used as the backbone because of its scalenohedral shape and narrow particle size distribution. The PCC particles were modified with Al-Mg-silicate and ZnS nanoparticles in four different blends. It was found that the light scattering of the modified PCC particle increased while keeping the diameter of the particle almost unchanged. It was important to keep the diameter of the particles the same as to not decrease the surface area of the particle, which would have lowered the surface area of the particles. The refractive index of the resulting particle increased the opacifying power of the coating layer due to the incorporation of micro deviations on the particles, which resulted in jumps in local indices between the air medium and nanoparticle sites on the PCC. The results of the experiments show an increase of light scattering of up to four times higher than that of the reference PCC was found.
Another new way of creating opacifying particles is by reusing the deinking residuals from paper recycle plants. The Pyroflex system is a series of controlled thermal and chemical reactions that selectively recover minerals and nanomaterials from a specific deinking residual (DIR)[20]. These residuals are then used to make white materials and other nanocomposites that can be mixed to optimize opacity, brightness, and porosity. The pigments are carbon-dioxide free and are considered carbon-neutral, making them eco-friendly.

According to the Pyroflex system, 20% by weight (bone dry) of all of the incoming waste paper leaves the system as deinking residuals. The Pyroflex plant can then convert 40% of these solids into minerals while the rest of the residuals are burned for their BTU value. By using materials created from the deinking process, mills that are able to incorporate this system can reduce landfill costs and virgin pigment costs. The savings from this system can range from a minimum of $2 up to $12 per ton of finished product. This savings could make the Pyroflex system a feasible way to produce opacifying pigments, if the cost benefits outweigh the initial investment.

Hollow-sphere synthetic pigments (HSP's) have also seen an increase in effectiveness to increase opacity, especially in the last 10 or so years. The spheres are made from an aqueous emulsion polymerization technique. These plastic pigments are hollow core structures that, when dried, increase the opacity of a coating. The shell diameters can be engineered from sizes ranging from 0.5 microns to 1.3 microns with inner void volumes ranging from 20-55% of the
entire particle volume[21]. The inner voids are what increase the light scattering ability by increasing the number of mediums the light has to pass through.

HSP's work as opacifiers, while also adding bulk, sheet gloss and ink gloss. The downsides to the use of these pigments are they decrease the density of the coating and are relatively expensive compared to other natural pigments other than TiO₂. HSP's are considered TiO₂ extenders rather than a replacement. In other words, HSP's can help spread the TiO₂ particles, potentially reducing the agglomeration of excess TiO₂ particles in the coating by using less TiO₂. This would make the remaining TiO₂ particles more efficient and reduce some cost while maintaining opacity.

Engineered silicate-based particles have recently been studied to increase the opacity in some base sheets by replacing pigment fillers. Depending on cooking conditions, the size, shape, and structure if the silicate particles can be modified. Therefore, the silicate particles can not only affect opacity but can be used to increase the bulking or glossing properties of the base sheet. The type of silicate particle that affects opacity the most is a long, fibrous, nano-particle. An example of these fibers can be seen in Figure 1.
The production of this type of silicate nano-fiber includes a hydrothermal reaction of silica and lime with high temperature and pressure. The diameters of these types of pigment particles can range from 50 to 200 nanometers and the length can range from 1 to 4 microns. The particles have an average ISO brightness of 95%, refractive index of 1.6-1.7 and an aspect ratio ranging from 1:10 to 1:50[22].
THESIS STATEMENT

This research will focus on the evaluation of a new Silica-based pigment for the replacement of TiO\textsubscript{2} in paperboard coatings. Factors such as size, shape, density, and particle size distribution will be taken into account for determining the feasibility of TiO\textsubscript{2} replacement. This research will look at the mass versus volume replacement of the TiO\textsubscript{2} with the silica pigment as well as the opacity, mottle, smoothness and other measurable properties of the coated paperboard.

METHODOLOGY

Five coatings were made and applied to a pre-coated, commercially produced recycled paperboard using a blade-metered Cylindrical Laboratory Coater (CLC). Four different coat-weights ranging from 8-26 g/m\textsuperscript{2} were applied for each formulation at 3,000 fpm. Target coat weights were 8, 14, 20, and 26 g/m\textsuperscript{2} (+/- 1 g/m\textsuperscript{2}). After conditioning to TAPPI conditions, the gloss, brightness, Tobias mottle, DuPont appearance, Sheffield smoothness, and L*, a*, b* color spectrum of the coated boards were measured before and after calendering. "TAPPI conditions" refers to the state of the atmosphere and length of time the samples are conditioned before testing. TAPPI's recommended conditions are a relative humidity of 50%, at 23 \textdegree C, for at least 24 hours. Scanning Electron Microscope (SEM) images were also taken of selected samples of similar coat-weight and different amounts of TiO\textsubscript{2} to visually determine if any differences in the surface characteristics between the reductions of TiO\textsubscript{2} in the coatings could be discerned.
The grammage of five uncoated and coated samples were measured using the CEM Smart 5 Moisture analyzer and the coat weights were determined gravimetrically. All of the tests performed were done at room temperature in accordance to Tappi standards when applicable. The gloss was measured with a Technidyne Profile Plus Gloss meter in accordance to Tappi test T-480. The results for the Sheffield roughness were obtained from the Technidyne Profile Plus Roughness/Porosity tester in accordance with Tappi T-538. The Technidyne Brightimeter Micro S-5 was used to measure the brightness of the samples as specified in Tappi T-452. The \( L^* \), \( a^* \), \( b^* \) values were tested by using a 500 series X-Rite Spectrodensitometer. The Mercury Porosimetry test used a Micromeritics AutoPore IV 9500 series which employed a vacuum of 50 mmHg to evacuate the air from the sample before pressurizing the chamber to 60,000 psi. The Dynamic Water Retention (DWR) test was run on a Paar Physica UDS 200 at room temperature under a vacuum of 270 mmHg. The gap between the spindle, model mp31, and the paper substrate was held constant at 3 mm and the shear rate was set and held constant at 100 Pa for each test. The DuPont Appearance Anaylzer was used to test the appearance (DAV2) values and the mottle (DMM). There were 8 slides used for the calibration of the DAV2 ranging from 28-191 at varying intervals. The same number of slides were used for the calibration of the DMM test with values ranging from 20-163 at varying intervals[23].
COATING FORMULATIONS

The amounts of components added to the formulation were based on their ratio to the total amount of pigments, expressed in parts per one hundred (PPH). PPH is based on the theory that all the parts of pigment will be equal to 100. From this point binder, additives, and rheology modifiers are related to 100 by giving them PPH that are usually much smaller. This method is useful to be able to relate all of the components that are in a coating before targeting a certain volume or amount of coating to be made.

Ti-Pure RPS Vantage was the titanium dioxide pigment and Kaomax was the clay pigment that was used in this work, produced by DuPont and Thiele Kaolin Company respectively. The pigments were dispersed for 20 minutes prior to making down the coating formulations. During this same time period, the pre-dispersed silicate nanofibers were also dispersed. The coating formulations were then made according to the formulation structure found in Table 3. Coatings 2-5 increase the amount of mass of the silicate nanofibers by 12.5% while decreasing the amount of TiO₂ by the same amount.
Table 3. Coating Formulations

<table>
<thead>
<tr>
<th>Coating Formulation</th>
<th>1 control</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Parts (PPH)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaomax*</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>TiO2</td>
<td>10</td>
<td>8.75</td>
<td>7.50</td>
<td>6.25</td>
<td>5</td>
</tr>
<tr>
<td>Silicate Nanofibers</td>
<td>0</td>
<td>1.25</td>
<td>2.50</td>
<td>3.75</td>
<td>5</td>
</tr>
<tr>
<td>Binder</td>
<td>21</td>
<td>21</td>
<td>21</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>Insolubilizer (wet/dry binder)</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Dispersant (wet/dry pigment)</td>
<td>0.12</td>
<td>0.12</td>
<td>0.12</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>Thickener</td>
<td>To Visc.</td>
<td>To Visc.</td>
<td>To Visc.</td>
<td>To Visc.</td>
<td>To Visc.</td>
</tr>
</tbody>
</table>

*Clay blend made by the Thiele Kaolin Company that is a mixture of premium #1 clay and calcined clay

The solids of the coatings were measured after all adjustments to viscosity and pH. The target solids of the coatings was 54% and was measured on the SEM Smart 5 solids analyzer. The pH of each coating was adjusted using a 27% solution of ammonium hydroxide to raise the pH to a target of 8.2. The pH was measured using a Corning 340 pH meter. The viscosities of the coatings were measured at room temperature using a Brookfield Viscometer, #4 spindle, at 100 rpm. The adjustments of the viscosity were made with a 3% solution of carboxymethylated cellulose (CMC) solution (by weight), until a Brookfield viscosity of approximately 1,200 cps was achieved.
RESULTS AND DISCUSSION

The objective of this work was to determine the feasibility of the replacement of TiO$_2$ in paper coatings with an untested silicate nanoparticle system. With that in mind, there are three categories in which to determine how effective these nanoparticles would be: physical testing, runnability in a production setting, and the economics. Having very little or no access to the two latter categories, this research looks at how the physical properties of coated paperboard are affected with the reduction of TiO$_2$ and the addition of the silicate nanoparticles both before and after calendering.

Gloss

Figure 2 shows the 75$^\circ$ gloss for the uncalendered samples. For each reduction in TiO$_2$, it can be seen that there is a general reduction in gloss when compared to the control coating. The highest gloss values were found for coating 1 (no TiO$_2$ replacement) averaging about 39. The lowest values were found for the 50% replacement(coating 5) averaging around 34. The loss in gloss with silica substitution is due to the change in pigment particle size. The silica pigment is a circular in comparison to the TiO$_2$ which are spherical.
As expected, the gloss increased upon calendering shown in Figure 3. After calendering, the values increased from the mid to high 30’s to the low to mid 50’s. Again, the control coating had the highest gloss compared to the other coatings but there was generally no change in gloss between coat weights.
Sheffield Roughness

The roughness of the uncalendered samples are shown in Figure 4. Taking into account the standard deviations, about 10 Sheffield Units (SU) for each coating, roughness did not significantly change with coat weight for all of the coatings. The smoothest coating was coating 2, having the lowest values, while the roughest coating was coating 5.

![Figure 4. Sheffield Roughness Uncalendered](image)

The Sheffield Roughness results improved after calendering for all of the TiO₂ replacements. The uncalendered roughness ranged from 80-140 mL where the calendered results ranged from about 40-70 mL as shown in Figure 5. The trend for the roughness after calendering is an increase in roughness with coat weight for a short period and then starts to decrease as the coating thickness increases.
The surface testing of gloss and roughness shows that there is very little change between each coat weight for a given coating. There are slight decreases in performance for each property with each coat weight increase, but after the samples are calendered there is little difference in roughness, whereas gloss decreases. The major difference is in the results between the coatings at a given coat weight. This suggests that there are changes to the surface of the coating that, as the silicate nanofibers are introduced, create a rougher surface that in turn reduces gloss.
**Brightness**

The brightness values for the uncalendered samples are displayed in Figure 6. The brightness values for all of the samples tested fell within the range of 83-89%. The control had the highest brightness and the 50% replacement of TiO$_2$ was lowest. Unlike gloss, brightness increased with coat weight for all of the replacement levels. This is due to better coverage of the darker base layer at the higher coat weights.

![Figure 6. Brightness Uncaledered](image)

As seen in the uncalendered results, the brightness increased with coat weight and decreased with nanosilicate substitution. Similar to the uncalendered samples, the brightness values ranged from 83-88% indicating that calendering did not affect brightness.
Figure 7. Brightness Calendered
Tobias Mottle

Tobias Mottle Testing was conducted to be able to numerically define the mottle present in the coated samples. The “Mottle” of a sheet is a term that generally describes an uneven appearance in color density. Recycled container boards usually have poor roughness full of high and low spots that can cause pooling of coating, thus higher and lower densities of coating. This ratio of darker and lighter spots determines the Mottle Index Value. During the Tobias Mottle testing, only two coat weights were measured for each coating. Tests were performed at the lowest and highest coat weights to confirm there was no real difference in mottle. Figure 8 shows no significant change in the mottle index with coat weight. Of the tested coatings, the 37.5% replacement (coating 4) was the most comparable to the control.

![Figure 8. Tobias Mottle Uncalendered](image)

The trend for the calendered samples shows a decrease in mottle with an increase in coat weight shown in Figure 9. This is most likely due to the amount
of clay accounting for the majority of the pigment in the coating and that at the coat weights chosen, the mottle is not greatly affected.

Figure 9. Tobias Mottle Calendered
DuPont Appearance

The DuPont Appearance Analyzer is a video image analysis machine that measures the uniformity of paper and paperboard products[24]. The DuPont Appearance Value (DAV2) and DuPont Mottle Measurement (DMM) values are dimensionless parameters that have low values for more uniform surfaces and high values for less uniform surfaces. The DMM is optimized to match human visual perception, while the DAV2 is used for fine scale variation, like a wire mask[25]. According to the handbook for this analyzer, the human eye starts to perceive mottle at a DAV2 of 59.

Figure 10 shows the results of the DuPont Appearance test and Figure 11 shows the results of the DuPont Mottle test for five samples containing coatings 1-5. Only one target coat weight was chosen for this test, 26 g/m², due to limitation of usable samples. The calendered samples had a higher appearance and mottle index value. For both of these test results, the calendered samples had higher values ranging from the 60's to the 90's. The uncalendered samples were much more consistent ranging from the 40's to the 50's with the exception of coating 5 which was about 65 for both tests.
The Tobias Mottle test did not pick up noticeable differences between the calendered and uncalendered samples, but when tested on the DuPont Appearance Tester there were differences. This is most likely due to better technology and the advancement of computers and scanners over the years. Both the DAV2 and DMM index values were better for the uncalendered samples. This can be explained by more air being entrained into the coatings thus increasing the overall
opacity power of the coating. However, like the Tobias Mottle testing results, there was little change between the coatings at a similar coat weight indicating that the silicate nanofibers compare to the refractive index of titanium dioxide.
L*, a*, b* Values

The optical color properties, L*, a*, and b*, are shown in Figures 12-17. L*, a*, b* values are used to define a point in a color space spectrum for all visible colors. The L values represent the lightness aspect, 0 = black and 100 = white. The "a" values indicate the difference between green and magenta. Negative values trend toward green while positive values indicate magenta. The "b" values show the difference between blue and yellow. Blue is indicated by negative values and yellow is indicated by positive values.

As a general trend for this test, the L values slightly increased as coat weight increased. The lightness values, L values, can be seen in Figures 12 and 13 for the uncalendered and calendered results respectively. The values for the calendered samples ranged from 93.5 up to 95.5, the control coating having the highest values at most coat weights. Compared to most of the uncalendered results, ranging from about 94-96, there was no significant changes in the lightness values. Lightness values increased with coat weight, indicating a better coverage of the paperboard.
With the exception of one outlier, the "a" value for all of the coatings averaged at about -0.68 for the uncalendered, see Figure 14. There was no noticeable differences in these values for any of the coatings. Figure 15 expresses the "a" values for the calendered samples. The "a" values decreased compared to the uncalendered results with most of the values ranging from -0.75 to -0.85. Unlike the uncalendered samples, the "a" values for the calendered samples decreased with increasing coat weight.
The uncalendered "b" values, shown in Figure 16, tended to decrease until the coat weight became sufficient enough to cover the substrate after which time they started to increase. Roughly around 14-15 g/m², the "b" values started to increase indicating that the coating became more yellow. The uncalendered samples ranged from 0.5 to 1.5 where the calendered samples ranged from about 0.8 to 1.8. As the coat weight increased, the "b" value increased as well, however, there was no distinguishable trend between all of the coatings. Figure 17 shows
the calendered results. These results show almost identical values as the uncalendered samples.

The $L^*$, $a^*$, $b^*$ values numerically describe the color of coated substrates. Though the difference may or may not be able to be seen with the human eye, there are some differences as measured on the spectrodensitometer. As would be expected as the coat weight increases, the $L$ values increases as well. Starting at an $L$ value of 94 and increasing to around 95.5 for the control coating, both
calendered and uncalendered samples tested similarly. The L values decreased with the addition of the nanofibers but by only about 1 point. Both calendering conditions resulted in values of roughly 93.5 on the low coat weights and 94.5 on the highest coat weight. The differences with the "a" and "b" values did not depend on the addition of nanoparticles or calendering but were dependent on the coat weight. As coat weight increased, samples became slightly more green and yellow as noted by the changes in the "a" and "b" values.
Dynamic Water Retention

The Dynamic Water Retention (DWR) for all five coatings are shown in Figure 18. The graph shows how long it takes the coatings to immobilize, meaning there is no longer enough water in the coating for particles to move past one another. The coatings are labeled as the amount of TiO$_2$ replaced in the coating formulation.

![Graph showing Dynamic Water Retention Test](image)

Figure 18. Dynamic Water Retention Test

There is a distinguishable difference between the control coating and the replacement coatings, however there is little difference between the replacement coatings themselves. The control coating is located furthest to the right, immobilizing around 600 seconds. The other four coatings immobilize in the range of 400-500 seconds with coating 2 immobilizing the fastest and coating 3 taking the longest.
The Dynamic Water Retention results show that there is difference between the control and replacement coatings. This is most likely due to the higher volume of TiO$_2$ particles in the coating layer densifying the coating filter cake during the draining process. The slower drainage rate leads to an increased time of immobilization. Having a higher immobilization time allows the coating to have a longer time to level after its application to the substrate. This helps to ensure a smoother surface before the coating sets. The exact differences between the coatings would need to be found by testing how the coatings react on a curtain coater and then correlations could be made. Changes to the time it takes for these coatings to immobilize could also be adjusted by modifying the rheology modifiers in the coatings.
**Scanning Electron Microscopy**

Scanning Electron Microscopy images were taken of five calendered samples that had a target coat weight of 26 g/m². Figure 19 shows coating 1 under 7,000x magnification. Due to the control coating containing two pigments and being mostly clay, the calendered sample has smooth surface. Figure 20 is coating 5, also at 7,000x, which has more pronounced voids in it. The implications of adding a higher fraction of different sized and shaped particles disrupts the packing structure of the dried coating. This creates a coating that has more air voids in it, thus making the coating more "open". There are rod-like structures that can be seen, which are part of the silicate nanofiber system. As the number of these particles increases, one would expect the openness of the coating to change as these particles do not pack the same. SEM images of all five of the samples, including the two shown below, can be found in Appendix A.
Figure 19. Control Coating - 7,000x

Figure 20. Coating 5 - 7000x
Mercury Porosimetry

Mercury porosimetry tests were performed to determine the influence of nanosilica on the pore size distribution of the dried coating layer. Three coatings were tested, the control, coating 3, and coating 5 (0%, 25%, and 50% reduction of TiO$_2$ respectively), all having a coat weight of 26 g/m$^2$. Figure 21 shows the pore size distribution for each sample.

![Figure 21. Mercury Porosimetry](image)

The results for all three coatings produced a bimodal graph with two distinct ranges of pore sizes. The first range varied from roughly 5-11 nanometers and the second range was from about 3-5 nanometers. The number of pores within these ranges varied for each. Coating 5 had the highest volume of pores in the 5-11 nm range while Coating 3 had the highest number of small pores. The control coating has fewer shallower pores. It is believed that the differences in
pore structure are caused by the differences in particle shape between the TiO2 and nanosilica fibers which resulted in a more open coating structure as the levels of TiO2 was replaced in the coating.

Figure 22 shows the particle size distribution for the titanium dioxide used in this work. As shown, the average particle size of the TiO2 pigment is around 200 nm.

![Titanium Dioxide Particle Size Distribution](image)

Figure 22. Titanium Dioxide Particle Size Distribution

Figure 23 shows the particle size distribution for the silicate nanofibers. The results show that there is a bimodal distribution of particles both in intensity weight and volume distributions. The first peak for both distributions is around 300 nm and the second peak is located around 700 nm. Given this information, it is understandable that the particle packing for each of the coatings would be disrupted upon substitution with the silicate nanofibers.
This would also account for an increase in the bimodal distribution in pores observed in the mercury porosimetry results.

Figure 23. Silicate Nanofiber Particle Size Distribution
**Mass versus Volume Impact**

Calculations were also done to look at the mass replacement versus the volume replacement of the TiO₂ in coatings 2-5. Using the specific gravities for each pigment; Kaomax(2.6), Titanium Dioxide(4.23), and the silicate nanofibers(2.4), the volume of each pigment was calculated. Table 4 shows the initial volume of Kaomax, TiO₂, and nanofibers in the control coating.

<table>
<thead>
<tr>
<th></th>
<th>Wet Weight (g)</th>
<th>Solids (%)</th>
<th>Dry Weight (g)</th>
<th>Volume (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaomax</td>
<td>2690.2</td>
<td>66.9</td>
<td>1800</td>
<td>692.3</td>
</tr>
<tr>
<td>TiO₂</td>
<td>278.9</td>
<td>71.7</td>
<td>200</td>
<td>47.3</td>
</tr>
<tr>
<td>Nanofibers</td>
<td>0</td>
<td>42.0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Each coating following the control had an increase of 25 dry grams of nanofibers while decreasing the TiO₂ equally. This would mean the fifth coating had 100 grams of TiO₂ and 100 grams of silicate nanofibers. However, the change in the ratio of volume between these two pigments was not equal; for every 10% of mass replacement, there is a 7.6% increase in volume. The overall volume change between each coating, including the clay, was found to be about 1%. This would indicate that in order to maintain the correct binder to pigment ratios, the latex in the formulations should be increased. An increase in latex would increase the cost of the coating but this price could be offset with the reduced cost in silicate nanofibers compared to the TiO₂ used.
CONCLUSION

The objective of this work was to determine the feasibility of the replacement of TiO$_2$ in paper coatings with a new novel silicate nanoparticle pigment. From the results of this study it can be concluded that the effectiveness of the silicate nanoparticles in a paperboard coating system would be effective at medium to low quantities. The nanoparticles are less dense than TiO$_2$ and could not be prepared at the same high solids content of TiO$_2$. Due to their low density, coatings containing these pigments will be reduced in density. Since papermakers sell based on weight, this means that a thicker coating layer would need to be applied. Also, the application solids of the coating may be adversely effected, which would require higher drying energy to be consumed. However, for most of the properties tested, little to no difference was found between the properties of the coated paperboard at replacement levels up to 50% on weight of TiO$_2$. Therefore, since the silicate nanofibers cost 1/8 the price of TiO$_2$, the cost savings associated with using the silicate nanofibers would be greatly beneficial to the coating formulator and paper industry.
BIBLIOGRAPHY

APPENDIX A

Appendix A contains the SEM images for 5 coated and calendered samples that have a target coat weight of 26 g/m². Figures 1-5 show the magnification of the samples at 7,000x to be able to see differences in the packing structure and surface characteristics of the different coatings. The figures contain, in order, the different coatings that were made 1-5. There is a clear difference between Figure 1 and Figure 5 but it can be difficult to see some of the differences between the other coatings.

Figure 1. Control Coating at 7,000x
Figure 2. Coating 2 at 7,000x

Figure 3. Coating 3 at 7,000x
Figure 4. Coating 4 at 7,000x

Figure 5. Coating 5 at 7,000x