

Pigmented aqueous barrier coatings

ANTHONY V. LYONS AND GREGG REED

ABSTRACT: The desire for more sustainable packaging has led to the development of new packaging materials that are fiber based. Aqueous coatings are a pathway to improve the recyclability of these materials. Pigments used in these coatings can improve the performance of the coating and reduce cost while further improving the recyclability. Mineral pigments are also considered to be compost neutral.

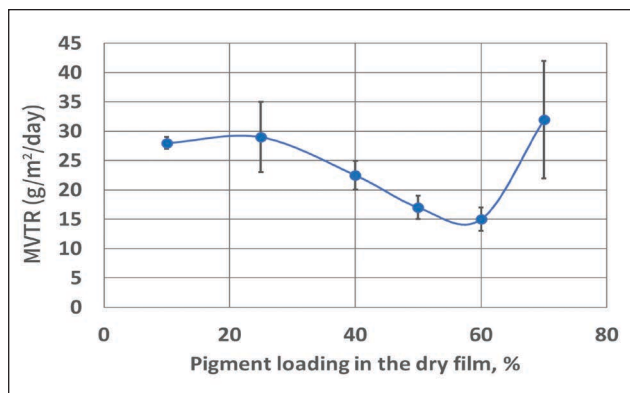
In this paper, we provide the reader a better fundamental understanding of the mechanisms by which pigments work in barrier coatings. A pigment's mineralogy and physical characteristics are important to how it will perform, and there have been recent pigment developments that improve coating performance. This paper shows that some pigments are better than others in particular barrier applications. Also, pigmented base or pre-coats can be used to prepare the surface for more highly functional coatings that go on top, improving the barrier function of packaging material and reducing overall cost. Finally, the converting operation is of major importance in driving formulation choices for barrier applications.

Application: This paper offers a review of the pigments used in these barrier coatings. The review includes the mechanisms by which they work and recommendations for pigments that are best to use for various barrier applications. This paper also provides examples of how the various pigments may perform in a barrier application.

There is a movement towards replacement of difficult to recycle and compost petro-based coating and containers. Wood fiber-based packaging is considered to be more sustainable. Wax, polyethylene, and polyethylene terephthalate (PET) coated packaging is still difficult to recycle and leaves behind a residue when composted.

Mineral pigments are considered to be neutral for composting (ASTM Standard D 6094-97 "Standard guide to assess the compostability of environmentally degradable non-woven fabrics") and make barrier coated fiber-based packaging easier to recycle when incorporated in the coating. These pigments can also enhance the barrier properties while reducing cost by replacing the more expensive bio-based and petro-based polymers that can be used in aqueous barrier coatings.

There are several pigments that have been or could be used in aqueous barrier coatings. Some of the more notable ones are kaolin, talc, calcium carbonate, and mica. More advanced coating applications have utilized bentonite and montmorillonite clays. Each has advantages and disadvantages, either because of their physical characteristics or surface chemistry. Platier pigments like mica, talc, and kaolin create a tortuous path in the coating. All mineral pigments raise solids for easier coating processability. The level of pigment must be optimized for best performance. When the critical pigment volume concentration is exceeded, then a more porous structure is created. At very low levels there is not enough of the pigment present to create a tortuous path when platy minerals are used. **Figure 1** shows data where various ratios of a barrier latex and a hyperplaty kaolin were evaluated for moisture vapor transmission rate (MVTR), demonstrating that there is an opti-



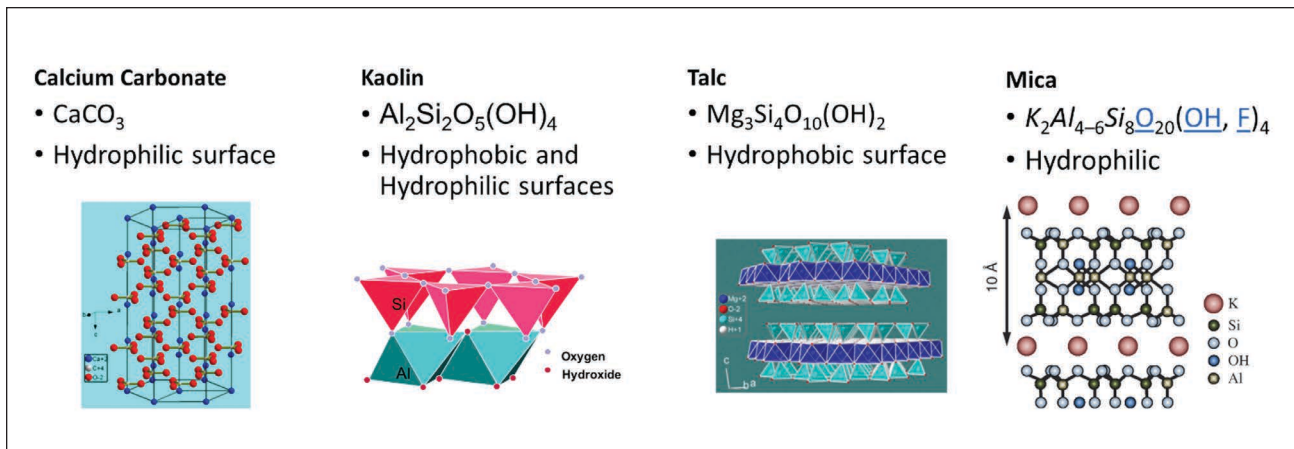
1. Optimization of pigment level for a formulation containing a hyperplaty kaolin and barrier latex (MVTR = moisture vapor transmission rate).

imum level [1]. For any of the minerals, this optimum level will depend upon the type of binder used. Another factor in optimizing the pigment level is crack at the fold. Platier pigments are notorious for causing crack at the fold. A break in the barrier coating film will undermine the barrier properties.

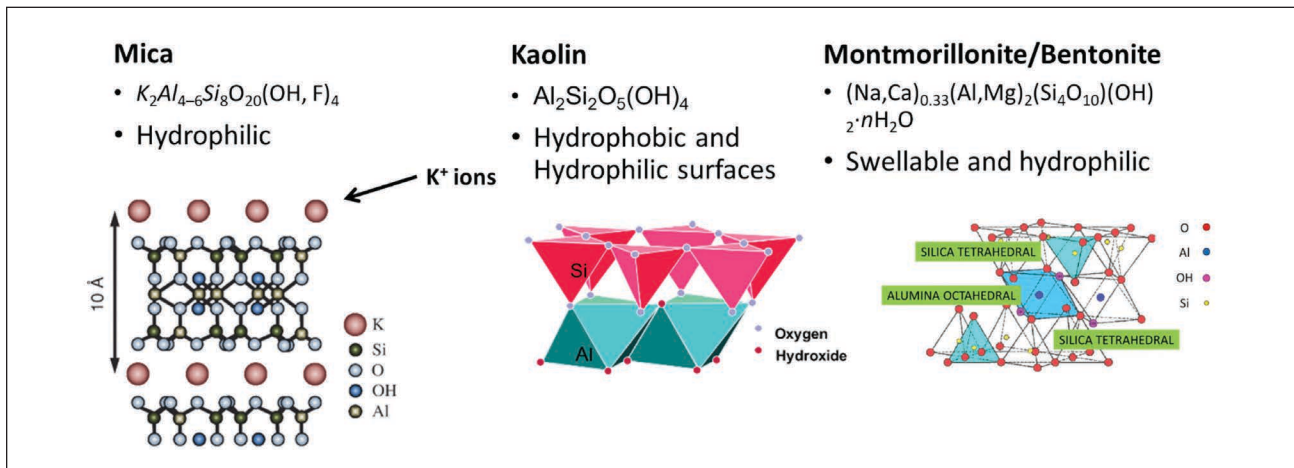
The coating process used can make a difference in the performance. Platier pigments perform better when the process aligns the pigments in a flow field. Blade, rod, and curtain coaters tend to align platier pigments so that they are more parallel with the surface.

The chemistry and crystal structure of mineral pigments determines whether they have hydrophilic or hydrophobic character. **Figure 2** illustrates the differences in the chemistry and crystal structure of the main mineral pigments that can be used in barrier coating applications. Kaolin

BARRIER COATING



2. Chemical and crystalline structure of mineral pigments create different hydrophobic and hydrophilic characteristics among them. Mica structure depicted is from [6].



3. A comparison of the chemistry and crystal structure between various phyllosilicate minerals. Montmorillonite/bentonite structure is from [7] and mica from [6].

(hydrophilic and hydrophobic) enhances oil barrier, talc (hydrophobic) enhances water and water vapor barrier, mica (hydrophilic) enhances oil barrier, and calcium carbonate (hydrophilic) can be used at a low level and can enhance the oil barrier.

Figure 3 illustrates the differences between the various phyllosilicate-type mineral pigments that can be used in barrier coating applications. Montmorillonite and bentonite clays are a favorite of the research community because they can be exfoliated into thin plates using a chemophysical method.

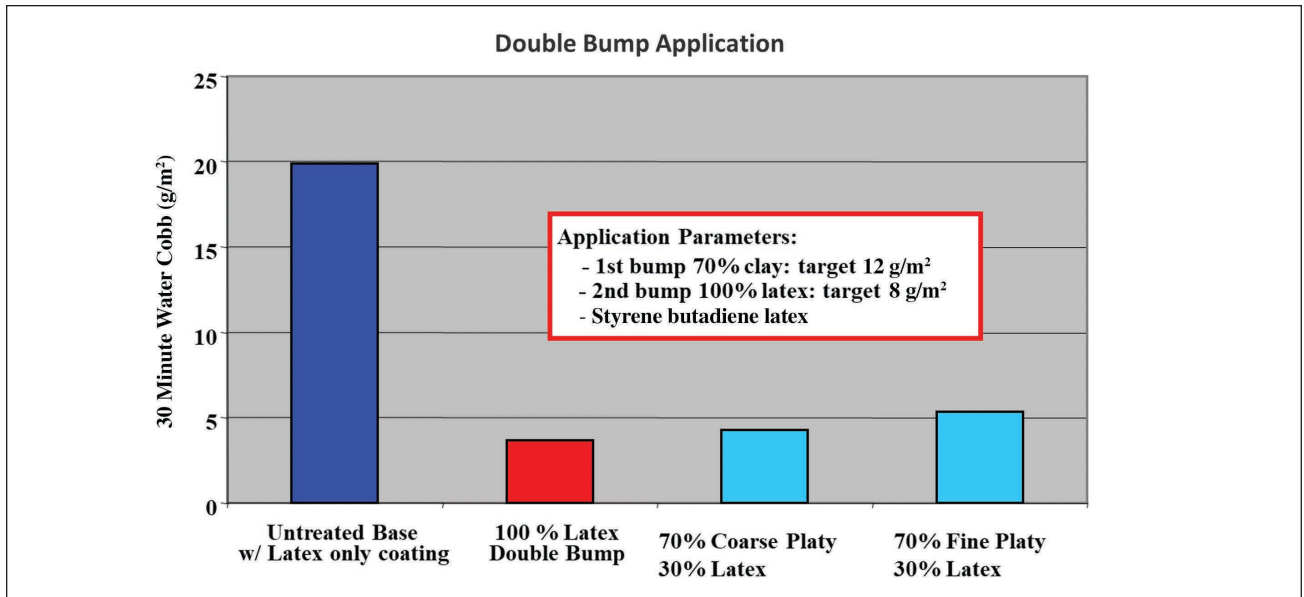
Besides being used in a functional barrier coating, the right pigment and binder combination can improve the smoothness of the base sheet. This then improves the efficiency of the barrier coating layer. The binder used in the base layer should also be functional for the particular barrier that is sought.

KAOLIN

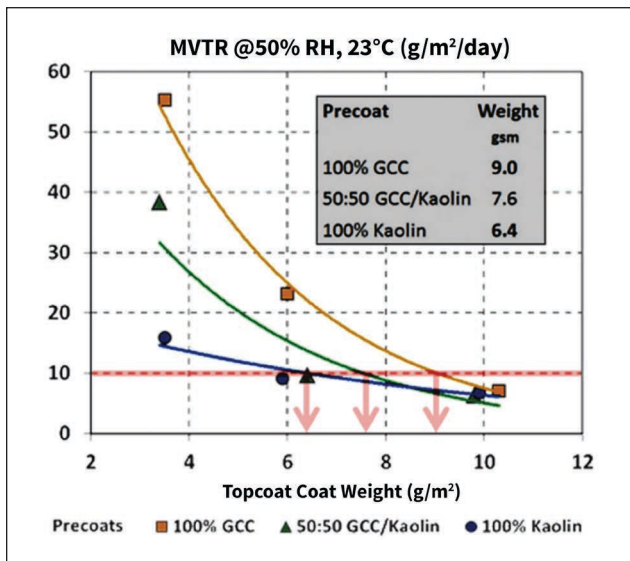
The chemistry and crystal structure of kaolin enhances oil barrier. There are hyperplaty kaolins available that produce

a tortuous path structure in the coating. When combined with binders like starch and polyvinyl alcohol (PVOH), an oil barrier can be created. Blocking occurs when using a low glass transition temperature (T_g) latex. When the coated product is reeled in a warm post-drying state, the low T_g latex acts like an adhesive to glue the paper layers in the reel together. A mineral pigment like kaolin can be used to control blocking when used as part of the formulation. There is a range of pigment levels that can be used, depending on the formulation, and in particular, which binder is used. Crack at the fold is a limitation, because the platy and stiff particles can interlock, creating a stiff coating. As demonstrated by the data in Fig. 1, the ratio of the pigment and binder needs to be optimized for maximum barrier.

One of the most effective and important applications of kaolin is as a precoat or base coat for preparation of a smoother and more closed surface for application of functional barrier coatings. This reduces the amount of functional barrier that must be applied, because the coating is held on the surface. **Figure 4** shows an example from



4. Illustration of the improvement in efficiency of the barrier coat to reduce the amount of latex required for the desired water barrier level.

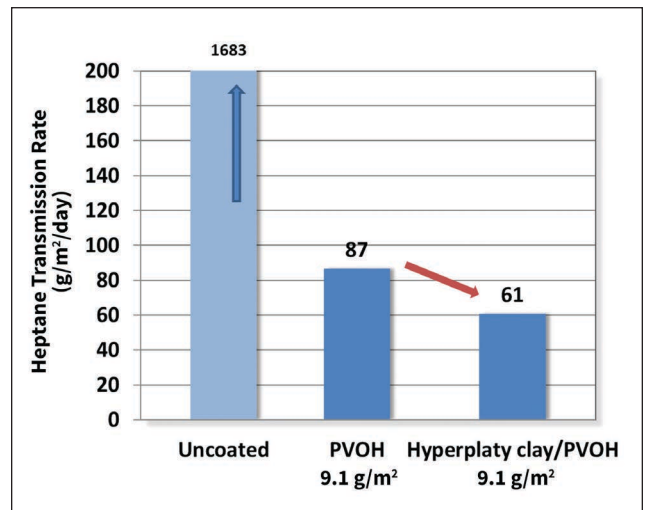


5. Kaolin use in a base coat can dramatically reduce the amount of functional top coat to achieve an MVTR target of 10 gsm/day (RH = relative humidity; GCC = ground calcium carbonate).

Imerys (Paris, France) where hyperplaty kaolin was used in a precoat to improve smoothness and make the barrier coat layer more efficient. The latex was a barrier styrene butadiene (SBR) type.

Figure 5 gives another example from Imerys where ground calcium carbonate (GCC), kaolin, and a 50:50 blend of kaolin and GCC were evaluated for their effect on the efficiency of the barrier top coat. To achieve a 10 gsm/day MVTR at 50% relative humidity (RH) and 23°C, 100 parts kaolin vs. 100 parts GCC in the formulation reduced the top coat by about one-third.

Kaolin can be effective in oil and grease barrier applica-



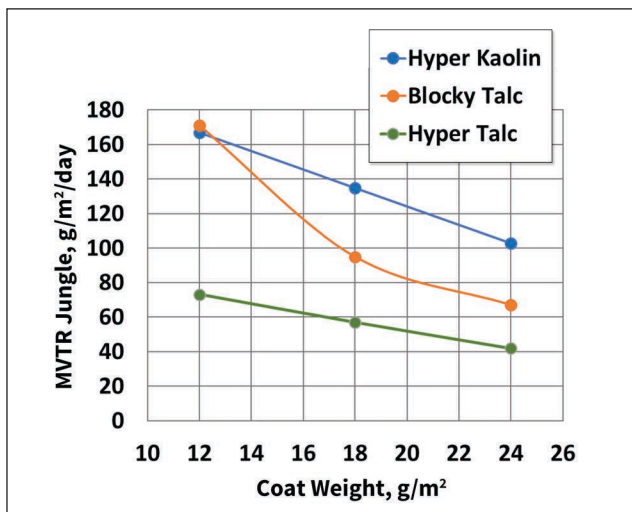
6. Enhancement of a polyvinyl alcohol (PVOH) mineral oil barrier coating by a hyperplaty clay.

tions. This is illustrated in **Fig. 6** from data generated in the Imerys Sandersville, GA, USA, laboratory, where a PVOH coating is further enhanced by addition of a hyperplaty clay.

TALC

The chemistry and crystal structure of talc enhances water and water vapor barrier because of the hydrophobic nature of the particle surface. Talc's platy character produces a tortuous path. This mineral pigment can also be used for control of blocking. Again, there is a range of pigment levels that can be used, depending on the formulation and binder. It is important to optimize the ratio of the binder and pigment to maximize the barrier while controlling crack at the fold.

BARRIER COATING



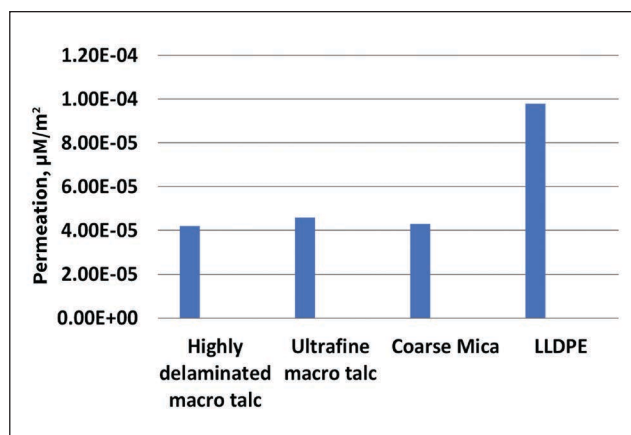
7. A comparison of blocky, platy, and surface chemistry of the pigment used for moisture vapor barrier. Hyperplaty talc gave the best performance (jungle conditions = 38°C at 90% RH).

A comparison is shown in **Fig. 7** of a blocky talc, hyperplaty kaolin, and a hyperplaty talc [2]. The effects of the platiness and the surface chemistry of the pigment are illustrated by this example. The formulation was 100 parts of a barrier latex and 100 parts of the mineral pigment.

CALCINED CLAY

Calcined clay is often used for thermal barrier applications. The structure of thermal paper is illustrated in **Fig. 8**. Calcined clay has a low density and self-contained air voids that slow the diffusion of heat. This is very useful in the production of thermal transfer and thermally activated papers. It is most often used in the precoat layer or in single layer coating for thermal transfer paper. This layer helps to retain the heat on the surface in order to better control the quality of the print.

The porous nature of calcined clay makes it a poor pig-



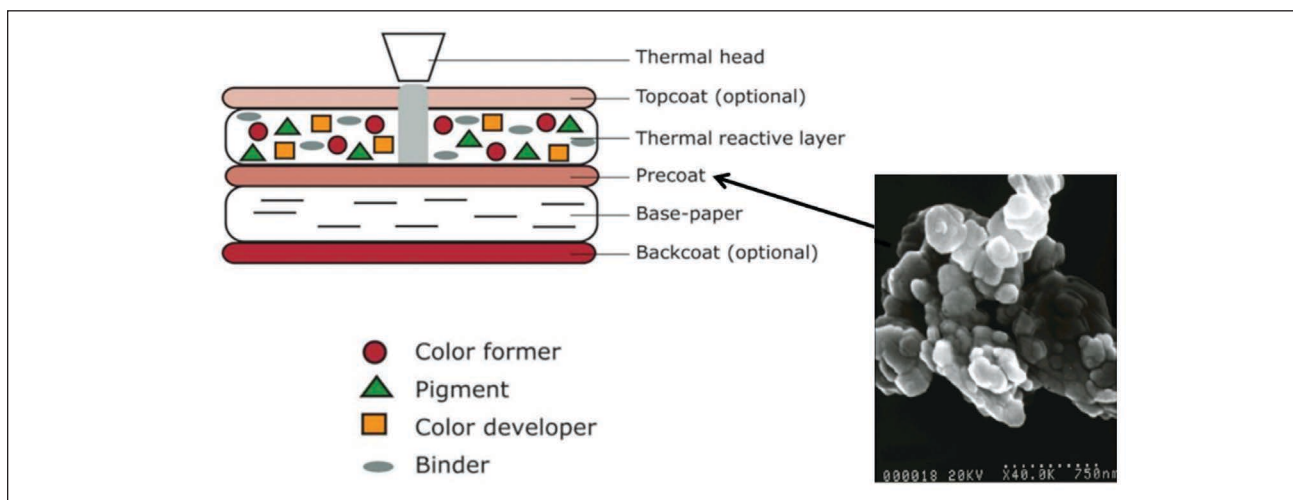
9. The performance of mica is comparable to talc in this mineral filled linear low density polyethylene (LLDPE) application.

ment for use in barrier coatings for water, moisture, oil/grease, and odor.

MICA

The chemistry and crystal structure of mica enhances oil barrier. It is a platy/flaky mineral that produces a tortuous path. Mica is a more flexible mineral than the other platy minerals, so crack at the fold is less severe with it. It can be used like the other pigments to control blocking. There is a range of pigment levels that can be used, depending upon the formulation. As with all of the mineral pigments, there is an optimum level for barrier and one still has to be on the lookout for crack at the fold. **Figure 9** shows how well mica works in comparison to talc [4]. This is not an aqueous barrier application, but the same sort of performance comparison can be expected. Mica is often used in architectural paints that are used to cover up various stains on a wall as a primer. The mica enhances the barrier to blooming of the stain through the dried paint.

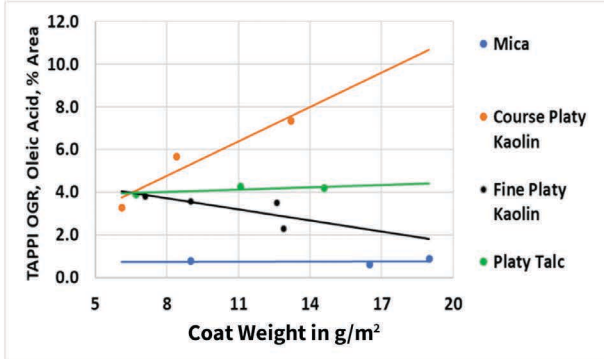
In an aqueous barrier coating, mica can enhance the oil



8. Calcined clay is used as a thermal barrier coat in thermal print papers [3].

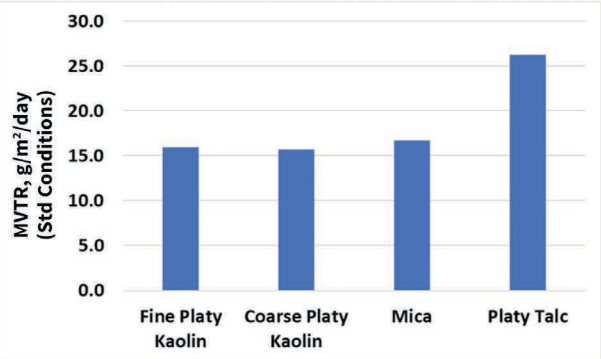
TAPPI OGR

100 parts pigment/100 parts barrier latex

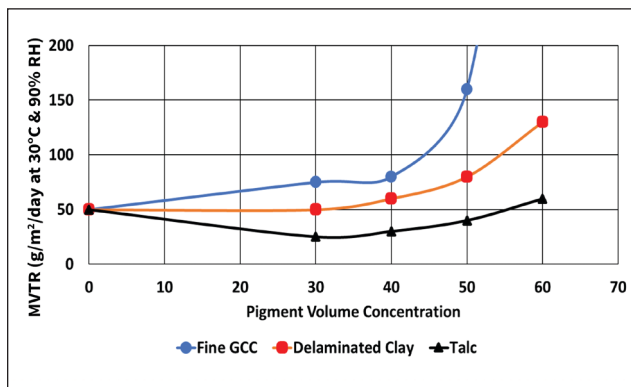


MVTR

100 parts pigment/100 parts barrier latex @ 10-12 g/m² coat weight



10. In this set of Imerys application work, mica gave the best performance for oil and grease resistance (OGR) with the barrier latex used in the study, as evaluated by TAPPI Standard Test Method T 559 "Grease resistance test for paper and paperboard," and maintained about a 16 g/m²/day MVTR under standard conditions (23°C at 50% RH).

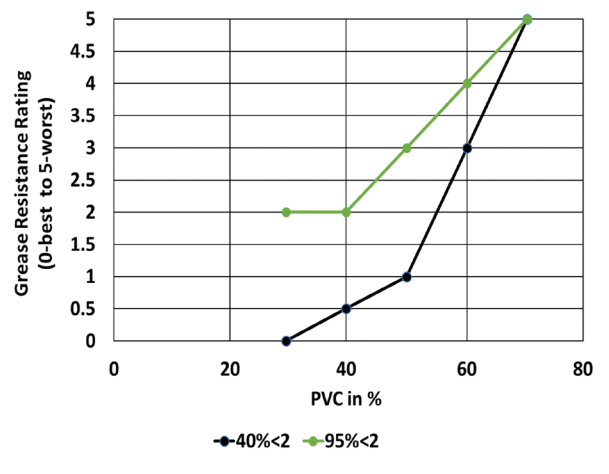


11. A comparison of MVTR for a fine GCC, delaminated clay, and talc is plotted as a function of pigment volume concentration (PVC) [2].

and grease and moisture barrier. **Figure 10** illustrates the potential performance of mica in these barrier applications.

CARBONATE

Calcium carbonate pigments, either GCC or precipitated calcium carbonate (PCC), can be utilized at low levels to extend the polymer. The nature of the surface of carbonate pigments lends itself to oil barrier applications like mineral oil barriers. Even for moisture vapor and water barrier applications, carbonate can be used at low levels to extend the binder used. Carbonates do not perform as well as the platier pigments do for flat stock. **Figure 11** shows how much better a delaminated clay and talc are for moisture barrier at 30°C and 90% RH on a flat stock. Upon creasing, carbonates can hold up better, because carbonate containing coatings typically tend to fold more easily as they are not as stiff as their platier pigment counterparts. Carbonate performance is not as dependent upon the coating process as the platier pigments are.

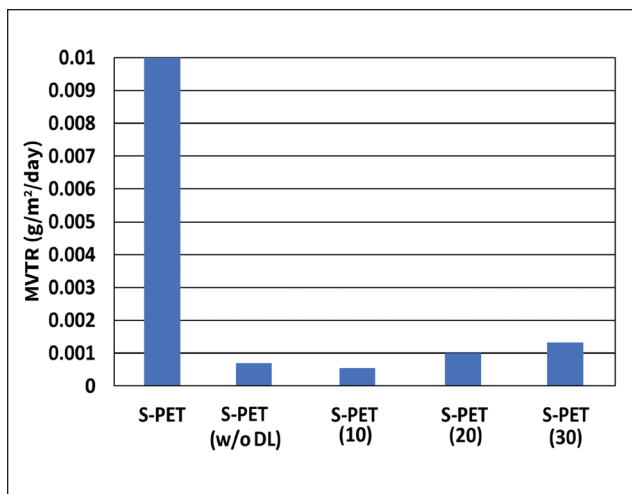


12. Comparison of a coarse and fine GCC on a flat surface using the grease barrier test on a flat surface after 180 min of oil exposure [2].

Coarser carbonates are better for barrier applications. It can be speculated that this may be related to the surface area of the particles being lower, thus freeing up more of the binder to make it more effective. This is illustrated in **Fig. 12**, where the grease barrier rating on flat stock is plotted for a coarse vs. fine GCC. Here is a description of the test used:

The grease resistance was estimated with colored turnip oil. Oil was poured into cups formed from samples with both flat surfaces and creases made with Patra hand creaser. A crease forms when paperboard is pressed into a groove with a rule. This causes deformations allowing the paperboard to fold easily without cracking. After certain time in-

BARRIER COATING



13. Nano-clay/epoxy resin composite coating dry laminated to a sputtered SiOx/SiNy PET film (S-PET) gives enhanced barrier properties in comparison with an uncoated S-PET film [5].

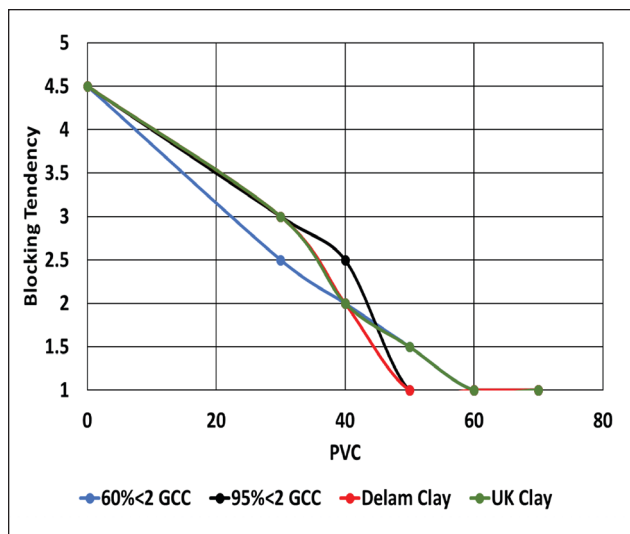
tervals the possible penetration of the oil was determined visually. 5 refers to total penetration and 0 to no penetration. Results of flat surfaces and creases (groove width 1.52 mm) with a folding angle of...180° are reported.[2]

MONMORILLONITE/BENTONITE

This clay mineral has gotten quite a bit of attention in academic circles. It is a swellable clay, which means that water molecules easily get in between the crystal layers and swell the structure. Various organic materials can then be imbibed between the layers, and then the composite is used in this manner. Or, after putting the mineral under shear, the layers of the crystal can be exfoliated or delaminated, resulting in very thin plates. It is mostly incorporated in nanoclay-polymer composite films and coatings, an example of which is shown in **Fig. 13** [5]. In this example, a nano-clay/epoxy resin composite coating was dry laminated to a sputtered SiOx/SiNy PET film (S-PET). The composite gave enhanced barrier properties in comparison with an uncoated S-PET film. S-PET(10), S-PET(20), and S-PET(30) were cured at 10, 20, and 30 min with the dry lamination process. The data point labeled without dry lamination (DL) was not cured. The dry lamination process was used to orient the exfoliated montmorillonite platelets.

CONVERTING CONSIDERATIONS WHEN USING MINERAL-BASED COATINGS

There are several factors to consider when utilizing mineral pigments in aqueous barrier coatings: heat seal-ability, crack resistance at the fold, blocking and sticking, printability, glue-ability, and mold/die release. As it always seems with paper coatings, it is not easy to balance all these properties. Heat sealing mineral-based coatings to fiber can be challenging. In particular, platy kaolin can cause a propensity for crack at



14. Blocking tendency of a pigmented coating with styrene butadiene as the binder decreases with increasing levels of pigment, no matter which kind of pigment is used [2].

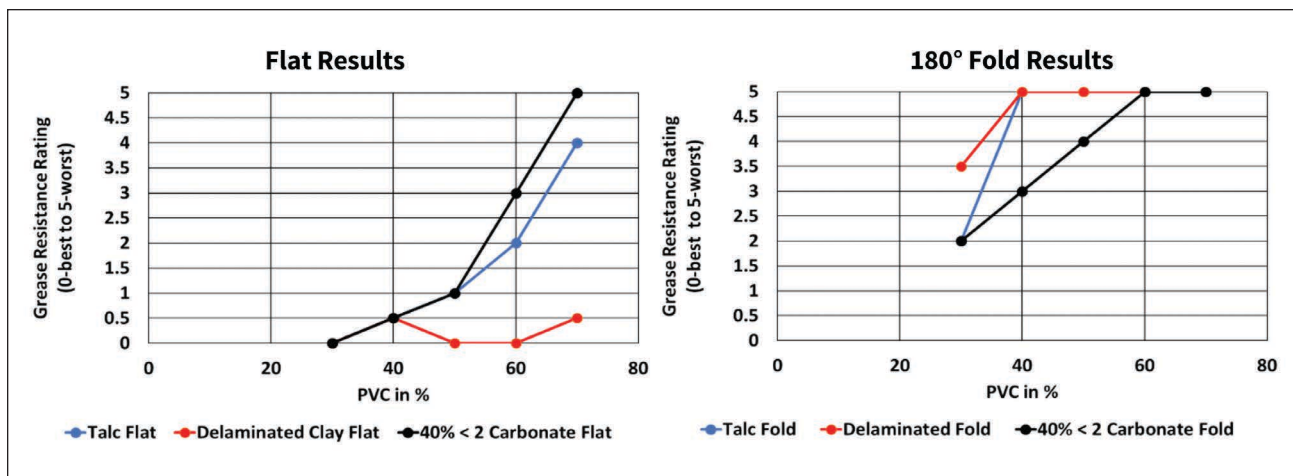
the fold. Reducing it often means using softer binders and at high levels. This is the right direction to take for heat sealing as well. What helps heat seal and crack at the fold can cause sticking and blocking in the roll. So, the level of binder vs. pigment and type of binder are important to optimize.

Figure 14 illustrates data generated on how blocking is reduced as the pigment level in the coating increases. This data was generated according to [2]:

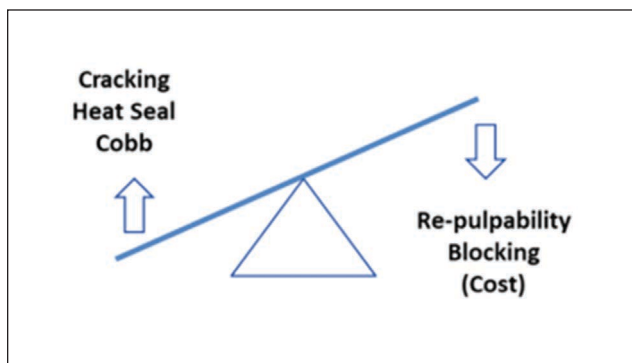
The blocking test was performed with a hydraulic press placed in an oven. The temperature during the 6-hour test was 50°C and the pressure was 15 Mpa. The coated side was tested against uncoated surface. After the samples had cooled, they were detached from each other and the blocking tendency was evaluated.

Evaluation of blocking tendency mentioned above was performed as follows: Rating 1—samples not attached to each other; Rating 2—samples attached, but only minor damage and can be easily separated; Rating 3—samples attached and <50 % of the area damaged; Rating 4—samples attached and >50 % of the area damaged; and Rating 5—totally blocked. As can be readily seen, the type of pigment was less important than the level of pigment in reducing the blocking tendency of the coating.

Creasing of the coated sheet in converting can result in crack at the fold. This reduces the barrier coating effectiveness. This is particularly noticeable for grease and oil barriers. The stronger the fold, the more that the barrier is broken down. **Figure 15** compares the results of the previously described grease barrier test using talc, delaminated clay, and coarse carbonate for a flat sheet vs. a 180° creased and folded one [2]. In a flat state, the delaminated



15. Grease resistance of flat sheet vs. strongly-folded sheet for a variety of pigments.



16. The balancing act in optimizing a mineral containing aqueous barrier coating system.

clay's physical and chemical advantages are readily seen. However, after folding, the carbonate can outperform other mineral pigments because of the reduced tendency for the coating to crack at the fold.

A common solution to strike a balance is to use multiple layers with various functionalities. As an example, a coating layer on the back side of cup stock could be designed for heat seal. The two opposing forces in balancing the barrier system design is that cracking at the fold, heat seal, and water resistance are together affected by changes in type and levels of the binders in the coating. Re-pulpability, blocking, and cost react in the opposite direction to any positive changes for the previous set of parameters. This is illustrated in **Fig. 16. TJ**

ABOUT THE AUTHORS

We studied this topic because there was a need for a comprehensive review of the role of pigments in aqueous barrier coating applications. There existed a lack of information on the fundamentals of the chemical nature and physical attributes for the wide variety of available pigments that can be used in these applications.

The most difficult part of this study was finding application research that supported our views on how these various pigments work. This research has its highest value in that it is the most comprehensive review of these pigments ever prepared.

We discovered that every mineral pigment available to the papermaker has a role to play in aqueous barrier coating applications, but some perform better than others in certain applications.

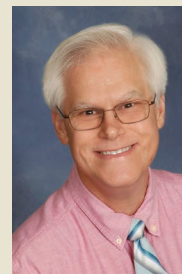
This work gives mills the fundamental knowledge they need to make the best choice of mineral pigment for a barrier coating application. There was a void in comprehensive information on these types of pigments as to how they work and are best used for barrier coating applications.

Our next step is to continue educating those involved in packaging design on how best to utilize these tools in coating formulations. There is also a need for continued optimization on how these pigments are used, such as the optimum levels of the pigments. For example, when is it best to just utilize them in surface preparation for a functional coating? And, are there mixtures of various pigments that can be used to optimize the performance?

Lyons is principal, Paper Lyons LLC, Lakewood Ranch, FL, USA. Reed is technical support leader, Paper & Board North America, for Imerys, Sandersville, GA, USA. Email Lyons at tonylyons15@gmail.com.



Lyons



Reed

LITERATURE CITED

1. Gittins, D.I., Skuse, D.R., and Khanna, Y.P., "Engineered performance pigments for moisture vapour barrier coatings," *PLACE Conf.*, TAPPI Press, Atlanta, GA, USA, 2008.
2. Vähä-Nissi, M. and Savolainen, A., "Filled barrier dispersion coatings," *TAPPI Coating Conf.*, TAPPI Press, Atlanta, 1999.
3. Koehler Paper Group, "Thermal technology," image, Koehler Paper Group, Oberkirch, Germany. Available [Online] <https://www.koehlerpaper.com/en/products/Thermal-paper/Thermal-technology.php> <04Nov2020>.
4. Imerys Performance Minerals, "Barrier properties," Imerys, Paris. Available [Online] <https://www.imerys-performance-additives.com/your-market/plastics/barrier-properties> <02Nov2020>.
5. Kim, H.G., Kim, E.H., and Kim, S.S., *Macromol. Res.* 26: 454(2018). <https://doi.org/10.1007/s13233-018-6055-6>.
6. Keller, A., Fritzsche, M., Ogaki, R., et al., *J. Chem. Phys.* 134(10): 104705(2011). <https://doi.org/10.1063/1.3561292>.
7. Caccamo, M.T., Mavilia, G., Mavilia, L., et al., *Materials* 13(5): 110(2020). <https://doi.org/10.3390/ma13051100>.

ABOUT THIS PAPER

Cite this article as:

Lyons, A. and Reed, G., *TAPPI J.* 19(11): 551(2020).
<https://doi.org/10.32964/TJ19.11.551>

DOI: <https://doi.org/10.32964/TJ19.11.551>

ISSN: 0734-1415

Publisher: TAPPI Press

Copyright: ©TAPPI Press 2020

[About this journal](#)