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Vinyl Acetate Coating Binders Making a Positive Impact in a Cost and Quality Sensitive Marketplace

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- Technological advancements have created new kinds of vinyl acetate-based coating binders
- Papermakers are quickly benefiting from not living in the past
- White pitch coagulants can manage white pitch deposition regardless of synthetic binder type

ABSTRACT

Paper coating binders comprising vinyl acetate are used extensively in North America for their contributions to brightness, opacity, porosity, and stiffness. Polyvinyl acetate homopolymer (PVAc) and copolymers of vinyl acetate and ethylene (VAE) are growing in demand because of their ability to extend or sometimes replace styrene butadiene (SB) and styrene acrylate (SA) coating binders. Besides typical performance properties, new criteria governing binder selection are emerging in the paper industry with increased emphasis on environmental impact and profit improvement. Today, new vinyl acetate technology has been developed to satisfy the undermet needs of the declining coated paper segment but there is an enduring fear of white pitch problems. This article will discuss the role of synthetic (latex) coating binders on white pitch formation and one way to effectively curb deposition on a paper machine namely by way of chemical treatment of the coated broke.

INTRODUCTION

The primary role of any paper coating binder (natural or synthetic) is to firmly bond the pigment particles to themselves and to the underlying substrate. Research efforts in the past were directed toward the development of new binders that not only possessed superior binding strength, but also contributed other differentiating characteristics to the coated surface. Recently, however, many paper mills have been concentrating more on curbing their spend and producing a consistent quality product than differentiation. Accordingly, coated paper and board manufacturers today are more open to diversifying their raw material portfolio in their quest of producing good quality, cost effective substrates, and this led to the development of modern day vinyl acetates and copolymers (e.g., PVAc,

VAE). Unlike SB and SA latexes, vinyl acetate-based binders are less costly on a price-per-pound basis and they've proven themselves to be good optimizers for said latexes even at disproportional dosages. PVAc and VAE's have many other notable properties too, for example, their contribution to fiber coverage and coating bulk which in turn can help reduce coating and/or packaging weight.

Unfortunately, the bad press associated with vinyl acetates, namely white pitch, has curbed their appeal *in coated paper applications only* due to past history as bad actors in the wet ends of paper machines.

White pitch is a very complex subject in the coated paper industry. A variety of authors have published articles relative to white pitch and many of these articles discuss the development or formation of white pitch, its composition, analytical techniques to detect its presence, and deposit control methods¹. Regardless of the content, each paper allows the reader an opportunity to better understand a particular aspect of white pitch. However, what continues to make white pitch so perplexing is that there are few documented disciplines which can account for the complete inhibition of troublesome white pitch deposits on the paper machine over an extended period of time. This statement is not meant to question the capabilities of papermakers, chemical suppliers, or academia. Indeed, there are a countless number of people in the pulp and paper industry that have spent exorbitant amounts of time and money studying and/or combating white pitch problems in one capacity or another and many will agree that each paper machine operates somewhat differently than the next and that each paper machine possesses chemistry unique unto itself and said complexity makes it very difficult to find the magic bullet.

In any event, many of our colleagues will agree that the source of this troublesome material is almost always the coated broke and studies have shown that a relationship exists between the concentration, size, and form of the colloiddally redispersed coated broke particles in a wet end (i.e., anionic trash) and machine runnability². Plainly, the lower the amounts of these "negatively-charged, wood pitch-like in size, but off-white in color" particles in the thin stock, the lower the machine's susceptibility to white pitch problems and vice versa. Today, turbidity, charge, and other analytical techniques are commonly used to help papermakers measure leading indicators like the above and subsequently mitigate or even preclude white pitch problems on their machines³. Although said test methods were readily available and in use many years ago, papermakers and suppliers seldom used the data to predict or control white pitch outbreaks. Rather, the data was mostly used to assess the efficacy of wet end chemicals namely those impacting retention, drainage, formation, and strength.

It was also well recognized by many gray-beards that coated broke comprising PVAc was more likely to cause white pitch problems than broke comprising SB. This common occurrence led many to study this issue in more detail and some have speculated that since most synthetic coating binders (SB, VA, etc.) maintain their adhesive functionality in the wet end and in the forming section of a paper machine, then altering, reducing, or eliminating the troublesome adhesive characteristic of a deposit was surely one key to success. With that in mind, new vinyl acetate-based coating binder technology has been developed *namely* VAE that renders itself less troublesome following its transformation into soluble and insoluble matter in the coated broke. This paper will examine VAE behavior versus SB and PVAc via

turbidity, charge and deposition testing. The effectiveness of coagulants to inhibit deposition and curb white pitch problems will also be discussed.

DISCUSSION

Let's begin with a layman's description of white pitch and the problems it can cause in a papermaking operation. During the papermaking process, some paper does not leave the mill as saleable paper. This includes trimmings, unfinished or damaged paper.

This paper is simply called "broke". Instead of discarding the broke, it is salvaged, pulped, and reintroduced to the wet end as part of the papermaking furnish (fibers, fillers, etc.). When "coated broke" is recycled, the coating, including the synthetic binders, enter the wet end in the form of small light-colored particles. Similar to wood pitch, these particles have strong binding properties and as a result can function as an adhesive or cementing agent for themselves and other materials in the system. White pitch is usually a collection of organic and inorganic materials common to the wet end of a paper machine and more often than not, sticky in nature. The actual percentage of the adhesive component (i.e., binder) can vary extensively. The higher the percentage, the greater the tendency for the white pitch agglomerates to form troublesome deposits on various parts of the machine causing holes, web breaks, problems with paper quality, and downtime for cleaning. The combination, if left unchecked, generally creates additional unsaleable paper (i.e., more coated broke) that needs to be managed/used up by the papermaker and most will agree that the higher the coated broke content in the papermaking furnish, the higher the potential for white pitch problems.

Next, let's discuss some of the conditions that promote white pitch deposition. Many chemistry texts submit that the concentration of reactants in a given environment will influence the rate of their reacting with one another or with other materials in the same environment⁴. Based on the preceding concept, one can assume that anything entering the wet end of a paper machine (solids, liquids, and gases) can influence a chemical reaction. These reactions can be advantageous or disadvantageous to the process. For example, an advantageous reaction can promote good sheet formation. A disadvantageous reaction, however, can trigger white pitch problems. To elaborate, high concentrations of particulates from the coated broke can place abnormal demands on the wet end. As we suggested to earlier, the higher the concentration of particles from the coated broke entering the wet end, the greater the potential to form deposits on the machine. Here, deposits occur because a critical saturation limit inherent to a particular system has been exceeded⁵. Exceeding the critical saturation limit can upset intricate wet end equilibriums or initiate the seeding of troublesome agglomerates. For instance, an influx of particles from the coated broke can transcend the efficiency range of the additive(s) typically used to control white pitch. Depending on the chemistry, surplus particles from the coated broke are free to deposit on the machine as a separate entity. Stated earlier, these particles can also form troublesome agglomerates with themselves or with other materials in the wet end. Particle influx can also tie up (deactivate) other additives typically used for retention, drainage, or strength⁶. This would be an example of surplus particles fueling an undesirable reaction in the wet end. This kind of upset almost always aggravates white pitch deposition. Last but not least, an influx of particles from the coated broke

can compromise the adsorption capabilities of the papermaking furnish namely the fibers. Here, the competition for reactive sites on the fibers or preferential adsorption of one component over another can leave an important ingredient without a task (i.e., musical chairs) and if the task is retention for example, then other runnability and quality problems can occur. Whichever the case, deposition occurs because the wet end cannot handle the overload which is primarily generated and subsequently fueled by the coated broke.

Stated earlier, a variety of measurement devices/tests are commonly used to monitor the white pitch potential of a machine. Low concentrations of particles in a wet end (e.g., turbidity) usually indicate the wet end is effectively managing the influx of particles from the coated broke and other sources. One can assume then, that the pitch control program is working efficiently. If a paper mill does not employ a pitch control program, then one can assume that the additives typically added for retention, drainage, and/or strength are preventing deposition by fixing the particles to the fibers. It's also quite possible that the wet end automation and chemistry is controlling deposition by stabilizing the particles (i.e., changing their size, shape, and/or nature) into innocuous forms which eventually will become incorporated into the continuous web of paper.

Emphasis must be placed on particulate form and size as well as quantity. Although low particle count values (turbidity) are generally more acceptable than high particle count values, a low number does not necessarily mean a system is trouble-free. Some additives or wet end conditions can promote gross flocculation or gross agglomeration of particles in the thin stock regardless of how many particles there are in the aqueous phase. Although a flocculation mechanism is highly desirable for retention, large flocculates can foul a machine when they approach or exceed a critical mass because they are more difficult to bind and/or bury than small particulates. Consequently, these agglomerates are prone to pick out of the sheet (and deposit) if they are not effectively bound to the web. Loose flocs are typically unstable, intermediate products, prone to deposition if they are only held together by weak chemical or physical bonds. Here, the shear forces in the head box or forming section of the machine can break apart the loose flocs into particles and fines that can build up on various parts of the machine or concentrate in the wet end where they can continue to fuel undesirable reactions.

One must also consider the soluble fraction (particularly from the synthetic binder) that is present in the system. Depending on the physical and chemical conditions in the coated broke tank, some dissolved binder (water soluble fraction) will pass downstream. In a closed white water system, this soluble fraction can increase in concentration until a critical saturation limit is exceeded and much like the undissolved (water insoluble fraction) mentioned earlier, upset the intricate wet end equilibriums and/or initiate the seeding of troublesome flocculates or agglomerates. The mechanisms may vary but the end results are always the same.

So, what can a papermaker do to reduce or eliminate white pitch deposition? As we all know, there is no simple answer. One must understand that the wet end of a paper machine contains all the ingredients common to white pitch; therefore, white pitch is always present in the system. The coated broke, in particular, furnishes the primary white pitch components namely redispersed coating particles

comprising the culprit synthetic binders. Paper coating compositions containing PVAc have generally been associated with white pitch problems (deposition, etc.) on machines producing coated printing paper (e.g., magazines, brochures). For this reason *and other changes in paradigm that occurred in the late 80's and early 90's namely the increased use of calcium carbonate to provide similar attributes afforded by PVAc like high coating brightness and blister resistance on web offset printing presses*, papermakers eventually stopped using this binder technology in their coating formulations.

Concurrently, a wide variety of wet end measurement techniques (charge, turbidity) and deposit control methods were evolving (dispersants, coagulants, detackifiers). Said advances in technology allowed papermakers the ability to manage the wet ends of their machines much better than ever before and in doing so, reducing deposition. Those that didn't are no longer business. White pitch problems, however, did not completely disappear even after most coating formulations settled on SB latex as their primary synthetic coating binder. Today, the unprecedented instability in SB prices and related issues with TiO_2 have compelled several coated paper mills in North America and in other regions of the world to examine vinyl acetate-based binders as an economical extenders or replacements for SB in their coating formulations and also because it is well known that vinyl acetate can help papermakers achieve maximum brightness and opacity⁷.

To help us learn more about the behavior of synthetic coating binders with respect to white pitch, we decided to benchmark the white pitch potential of SB, PVAc, and VAE using three tests; turbidity, charge, and a deposition technique. Additionally, we screened the performance of two coated broke additives namely coagulants under acid and alkaline papermaking conditions.

The coated hand sheets for the following series of experiments were prepared at lab scale. The base paper was from an LWC (lightweight coated) mill and it comprised a mixture of kraft and groundwood pulp. Said substrates were coated with a formulation comprising delaminated and calcined clays that were bound with equal amounts ethylated starch and SB as a cobinder, VAE as a cobinder, or a 50/50 blend of SBR and PVAc as a cobinder. We did not prepare/test hand sheets containing 100% PVAc because of the technical limitations of this approach in LWC offset applications. The SB was a high strength (carboxylated) binder typically used in coated offset paper applications having an onset glass transition temperature (T_g) near 0°C . The VAE was patent-pending (new) coating binder technology that is quickly gaining acceptance in similar applications. It had the same T_g as the SB. Likewise, the PVAc was new (high molecular weight) technology that supplanted the older lower molecular weight versions that were commonly used as cobinders with SB many decades ago. In this study, pigment and binder levels were held constant as was coating weight and finishing. The coated substrates were subsequently repulped in a high speed blender for approximately 15 seconds at 0.5% consistency.

We chose to measure charge and more specifically zeta potential via a Mutek zeta potential analyzer. Our rationale for measuring zeta potential instead of conducting charge demand titrations will be explained later in this report. Turbidity was measured using an HF Scientific Turbidimeter. Charge and Turbidity samples were passed through Whatman CR4 filter paper before any measurements were taken and so only the filtrate was tested. Here, we focused on the aqueous phase because of its role as

a carrier or the vehicle for the most perceived troublesome components making up white pitch i.e., redispersed synthetic binder coming from the coated broke. The laboratory test for measuring white pitch deposition was an NC State method that employed detachable preweighed nylon tabs circulating inside a blender cup comprising mixed pulp and or broke at high rates of speed for several minutes. At the end of each test, the nylon tabs were removed, oven-dried, and then reweighed to measure the weight of the deposits. Here, the repulped samples were tested as is at 0.5% consistency.

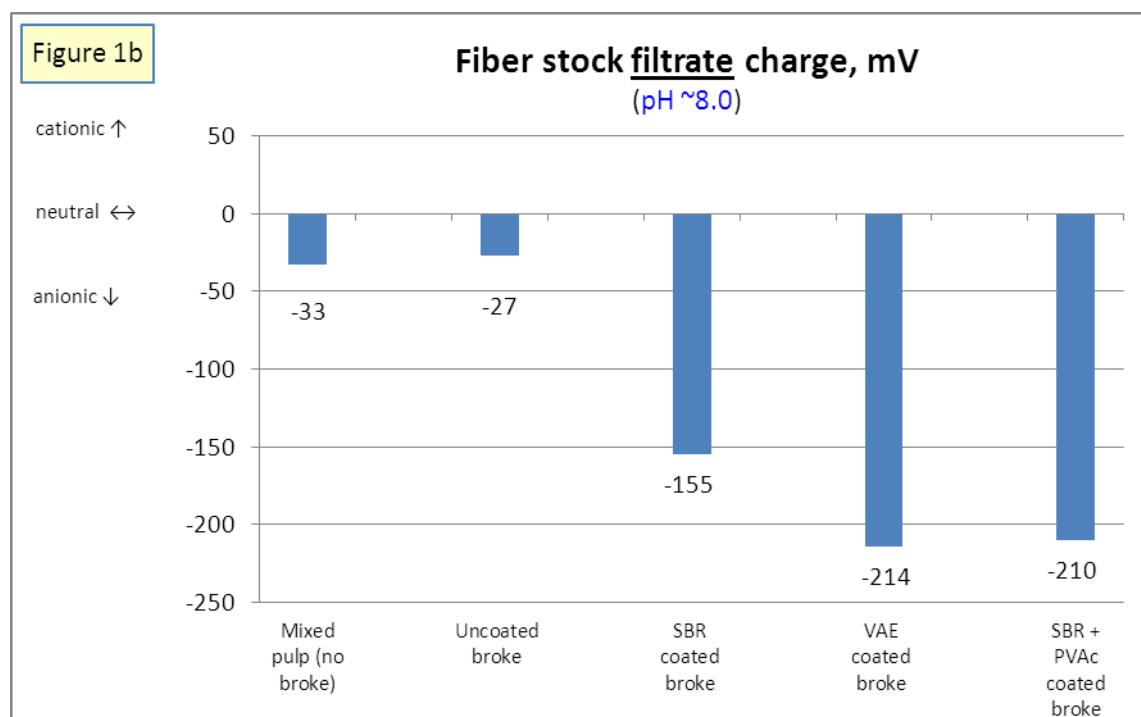
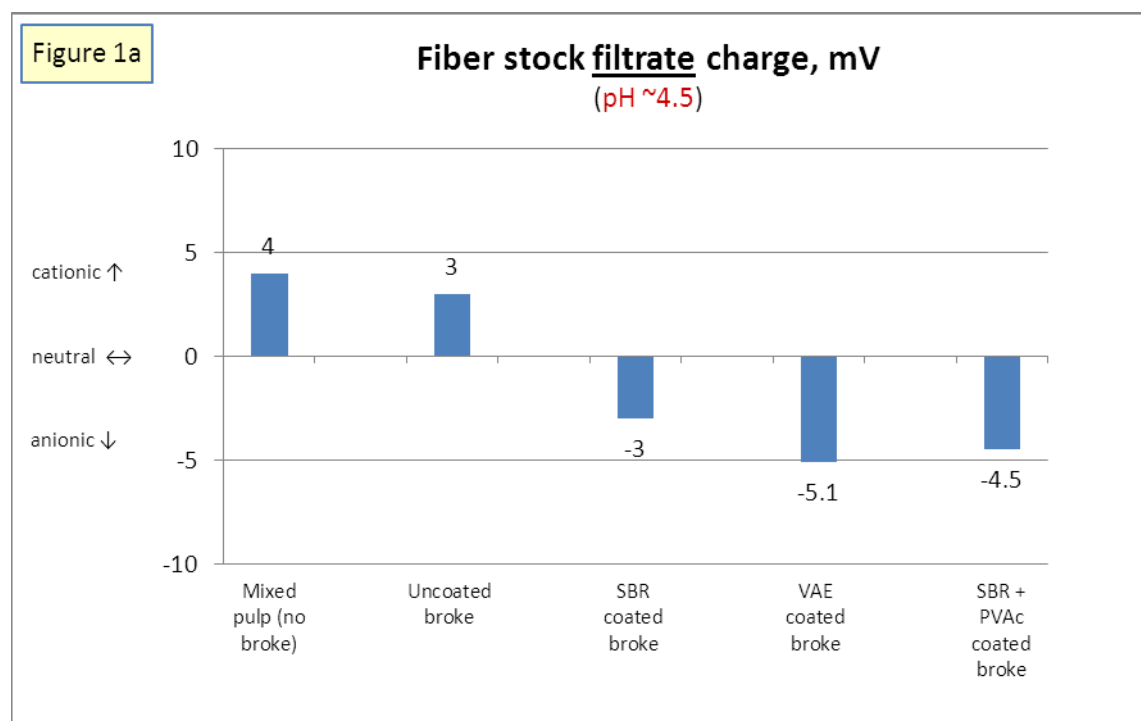
Lastly, all the tests were run at room temperature and therefore did not reflect typical papermaking conditions. However, since all the synthetic binders were thermoplastic in nature, we presumed that the amount of deposition would probably increase with increasing temperature due to polymer stickiness.

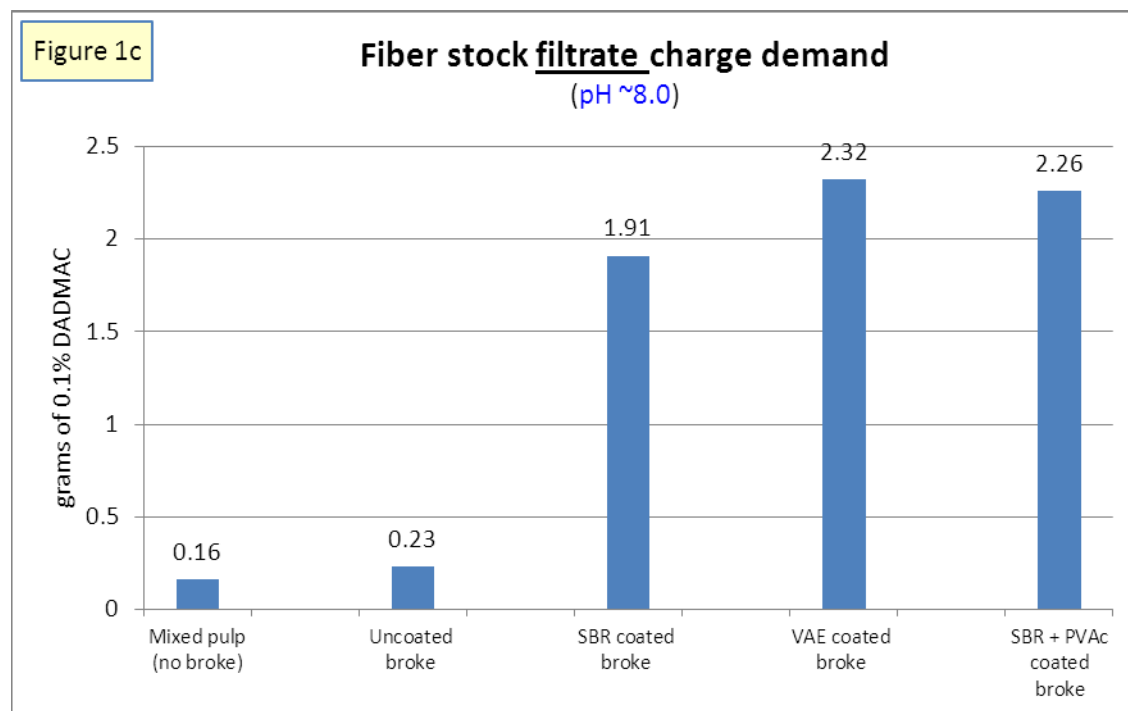
Other caveats: Statistical analysis of the results was not possible because only one experiment was conducted for each test condition. Rather, we took the arithmetic average of two samples for each experiment. Clearly, a well-designed DOE would have allowed for better analysis and interpretation of the results, but this study would have required more time than necessary to satisfy this simple benchmarking objective.

RESULTS

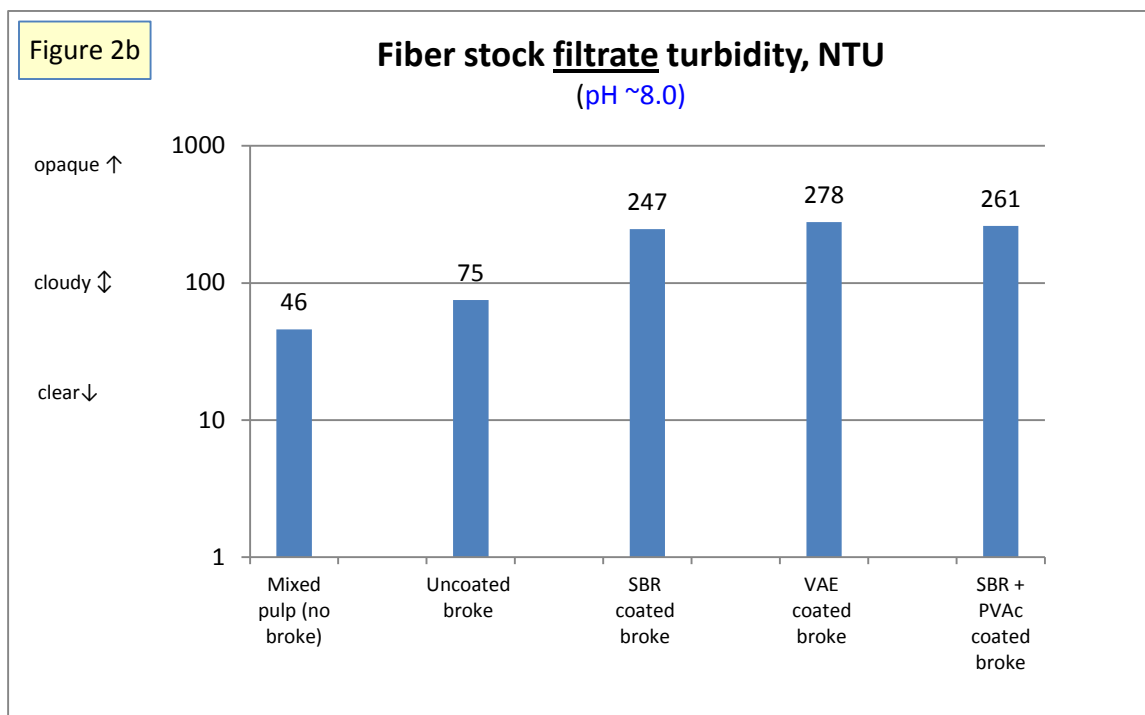
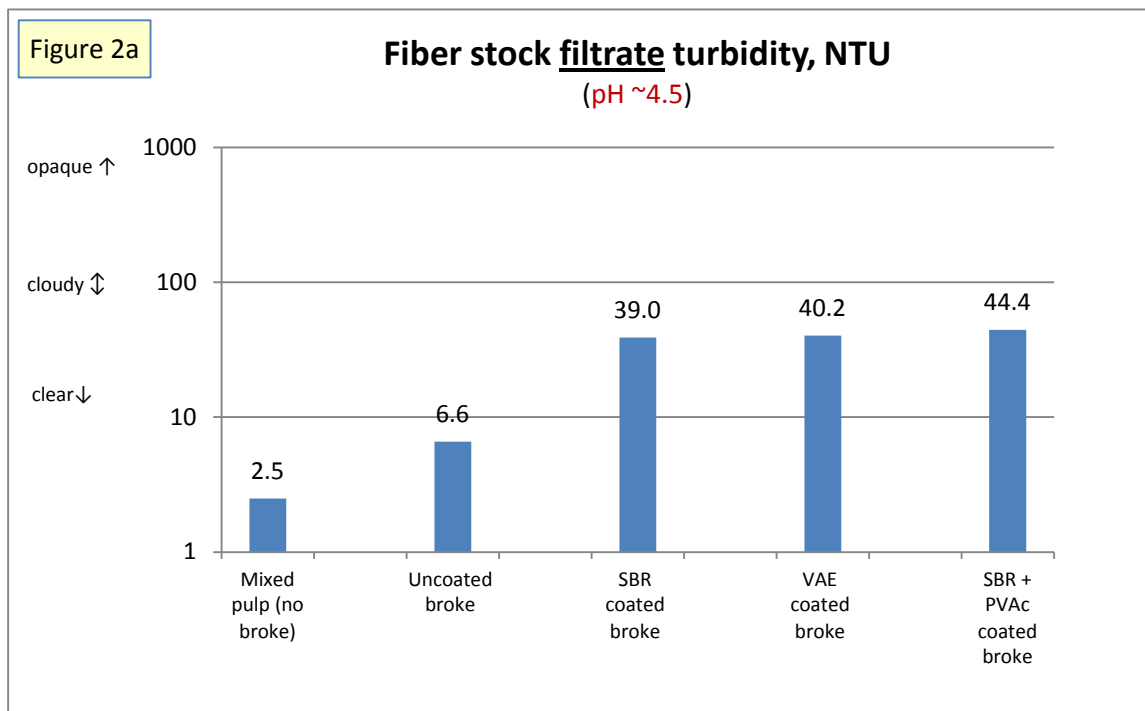
Our opening studies compared mixed pulp with uncoated broke and coated broke. The coated brokes were further differentiated by synthetic binder type namely SB, VAE, and the SBR/PVAc blend. The pH of the filtrates was either 4.5 or 8.0 to simulate acid or alkaline papermaking environments. Results are presented in Fig 1.

Figures 1a and 1b illustrate the charge of the preceding filtrates. It shows that the charge of the uncoated broke was comparable to the charge of the starting papermaking mixed pulp. Under acidic conditions, both filtrates were mildly cationic (i.e., positively charged). Under alkaline conditions, both were anionic (i.e., negatively charged). Additionally, the charge of all three coated brokes was significantly more anionic than the mixed pulp and the uncoated broke and here too, the alkaline filtrates were more anionic than the acidic filtrates. Figure 1c explains our rationale for choosing Zeta Potential as our charge measurement in this study. Although charge demand titrations are considered by some to be more effective indicators of system charge, we chose zeta potential because very small amounts of the positively charged polyDADMAC (diallyldimethylammonium chloride) titrant over-cationized the alkaline filtrates and prevented us from seeing any significant differences among the coated brokes. Zeta Potential (mV), on the other hand, allowed us to distinguish among the systems being tested and the data showed that coated brokes containing VAE or the SB/PVAc blend were more anionic than the SB. Most likely, residual surfactants coming from the vinyl acetate films influenced this test result. Further, the anionic charge of the VAE coated broke was comparable to the charge of the SB/PVAc blend.



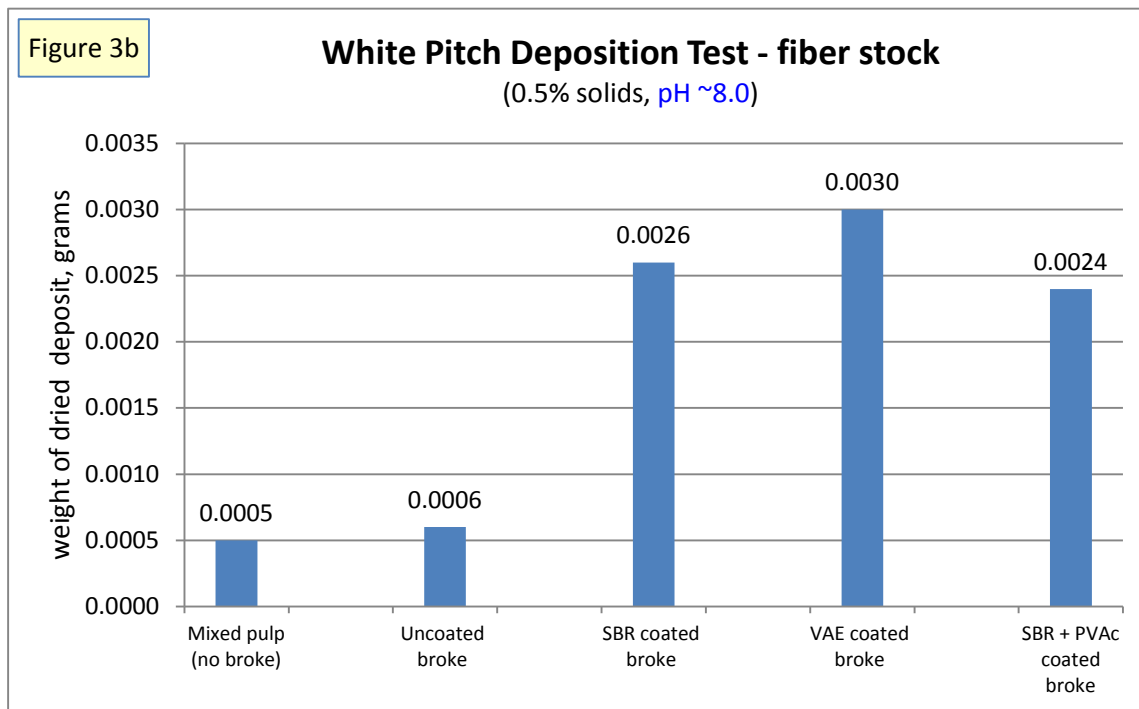
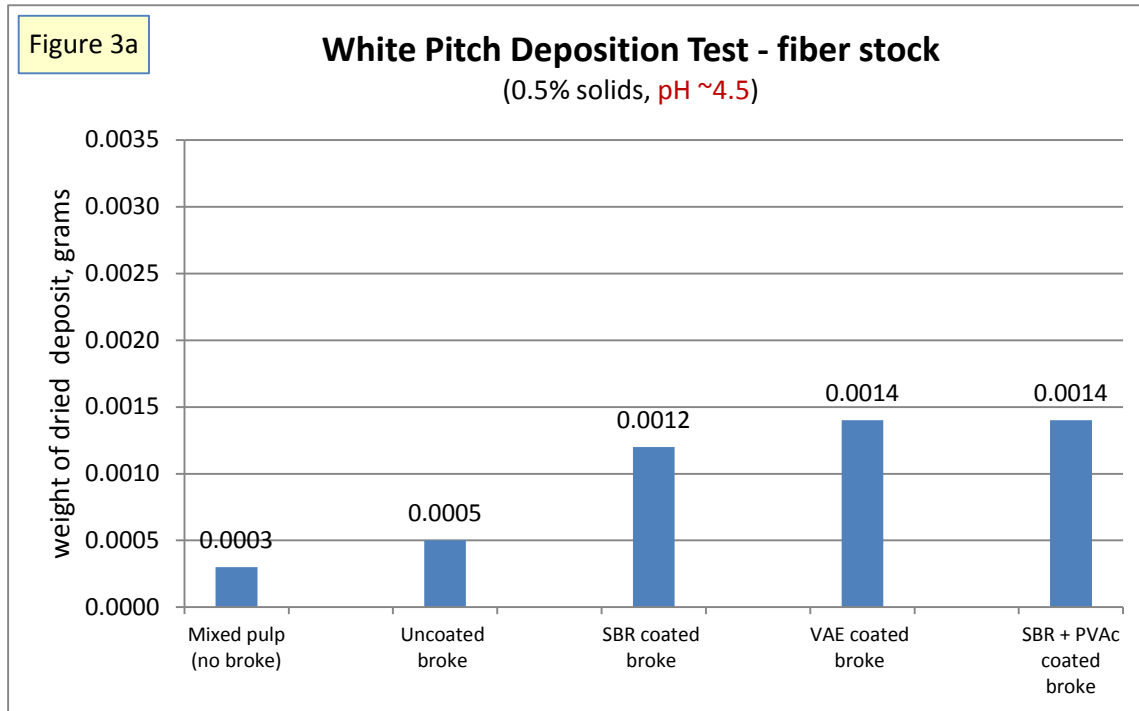


Figures 2a and 2b show the turbidity of the mixed pulp and the various brokes in terms of Nephelometric Turbidity Units (NTU) which is data based on light scatter. Here, the mixed pulp filtrate had slightly lower turbidity than the uncoated broke filtrate and the difference was most likely caused by the generation of fiber fragments and fine particulate matter during repulping (broke) process. The repulped coated sheet filtrates generated higher turbidity values than the uncoated substrates and this result was most likely influenced by the redispersed coating fragments that passed through the filter paper. Similar to the outcome of the preceding charge tests, the alkaline papermaking environment generated significantly higher turbidity values than the acidic environment. Unlike the charge results, there was no significant difference in turbidity among the synthetic binder systems. All behaved comparably.



Figures 3a and 3b depict the amount of white pitch deposits that came from each fiber stock. In this study, deposit weight increased with increasing papermaking pH. The mixed pulp and the uncoated broke had lower deposit weights than the coated brokes confirming role of the coating.

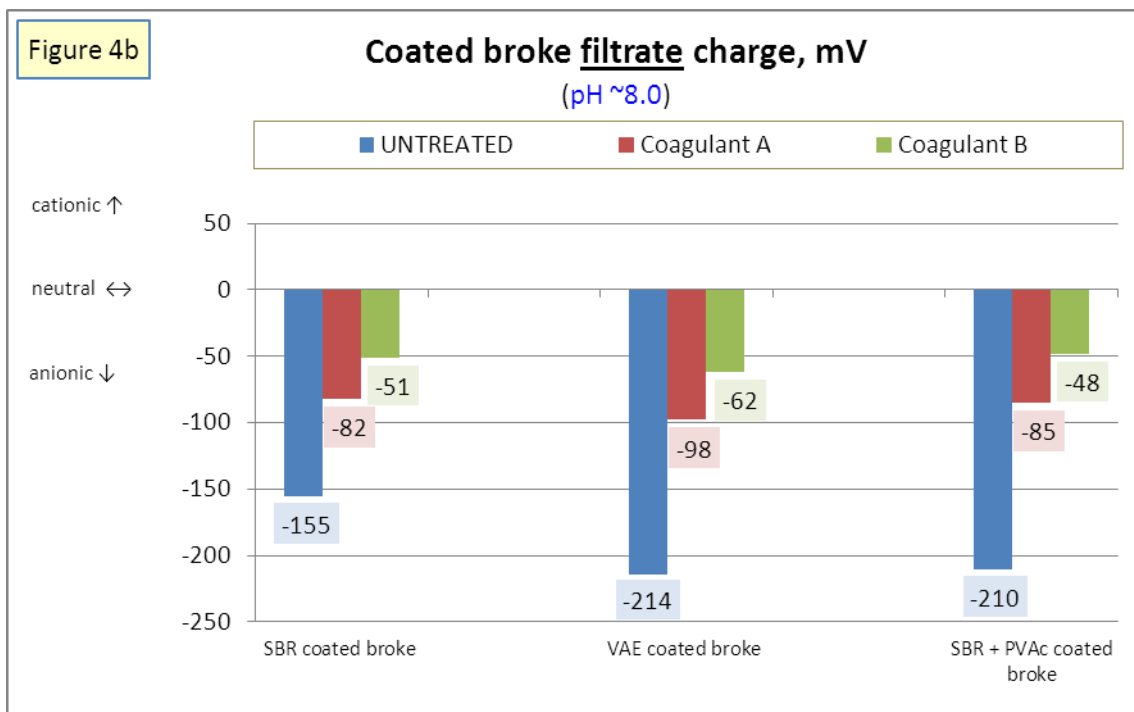
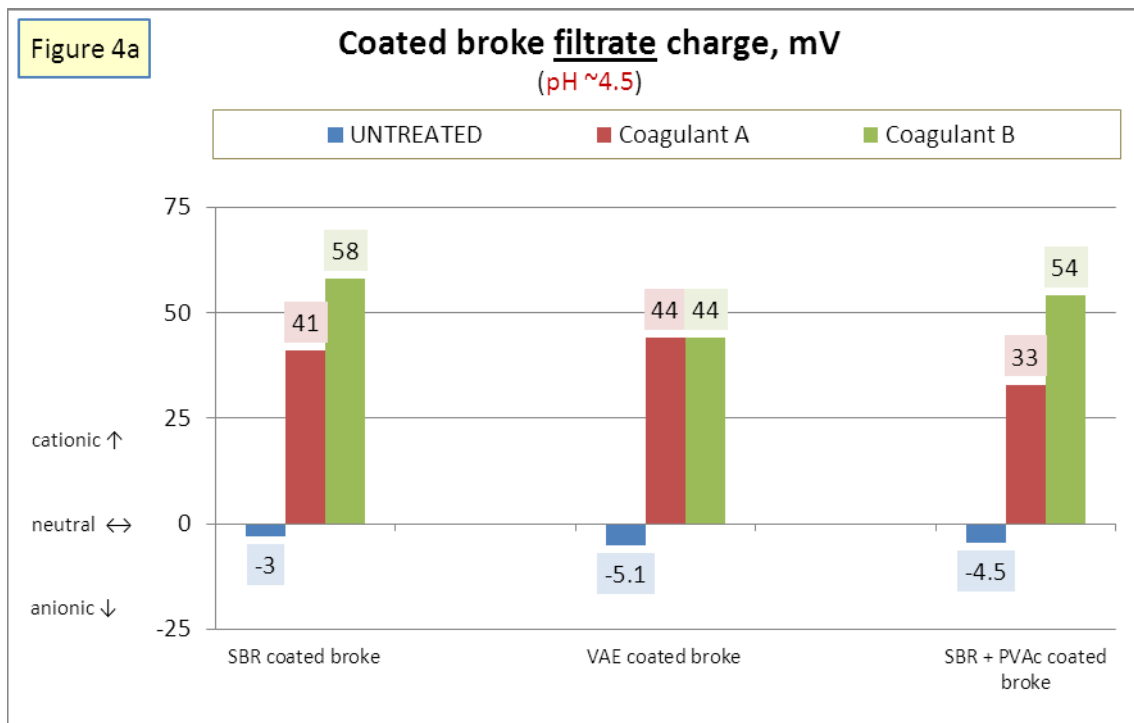
We can also infer from the data that the higher deposit weights for the coated brokes were attributable to the adhesive nature of the redispersed synthetic binders. Here again, all three binder systems behaved comparably.



Based on the results from this first series of studies, it was decided to proceed with an evaluation of chemical methods typically used to control white pitch problems. Today, several white pitch treatment programs exist. Some are designed to disperse white pitch in order to render it less troublesome, while others are designed to fix white pitch to the fibers so it can be incorporated into the web. There are also a few programs designed to stabilize white pitch in order to render it less tacky or less likely to form sticky deposits. From a chemical standpoint, the predominant approaches are dispersants, fixatives or coagulants, and detackifiers. The most successful programs, however, employ technology that is capable of anchoring and binding troublesome white pitch components to the fiber, preferably in the thick stock, so that the additives typically used to control retention, drainage, and/or strength can do their own job unabated in the thin stock.

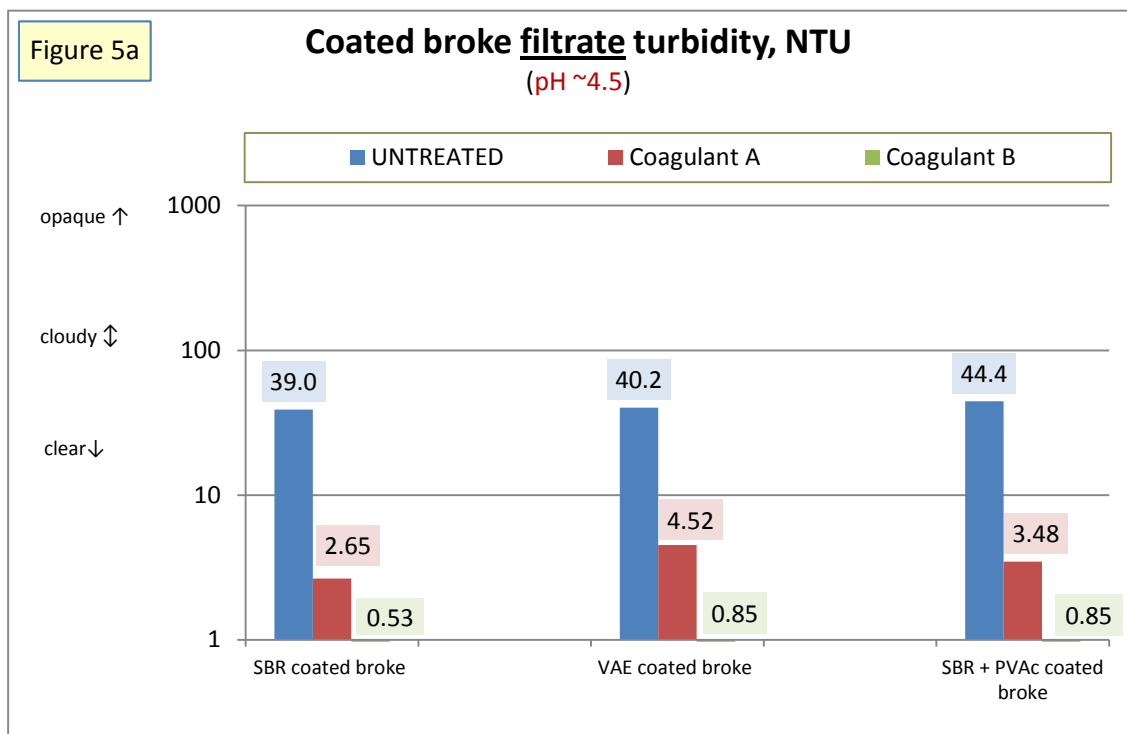
Hence, two coagulants were examined in this next series of experiments. One was a low molecular weight, high charge, cationic coagulant. The other was a medium molecular weight, medium cationic charge, hybrid coagulant. We chose these two chemistries because they worked well in the field as deposit control agents. Given the scope of this study, we did not examine any alternative products nor was there any reason to believe that other treatment regimens wouldn't work just as well either. The chemical addition range for these coagulants was 1 to 4 lbs. /ton as prescribed by the supplier. For this benchmarking exercise, we simply chose to add 2 lbs. /ton to the coated broke only. Untreated samples were included as controls for each coated broke system being tested namely SB, VAE, and the SB/PVAc blend. Here again, we tested the filtrates for charge and turbidity under acid and alkaline conditions.

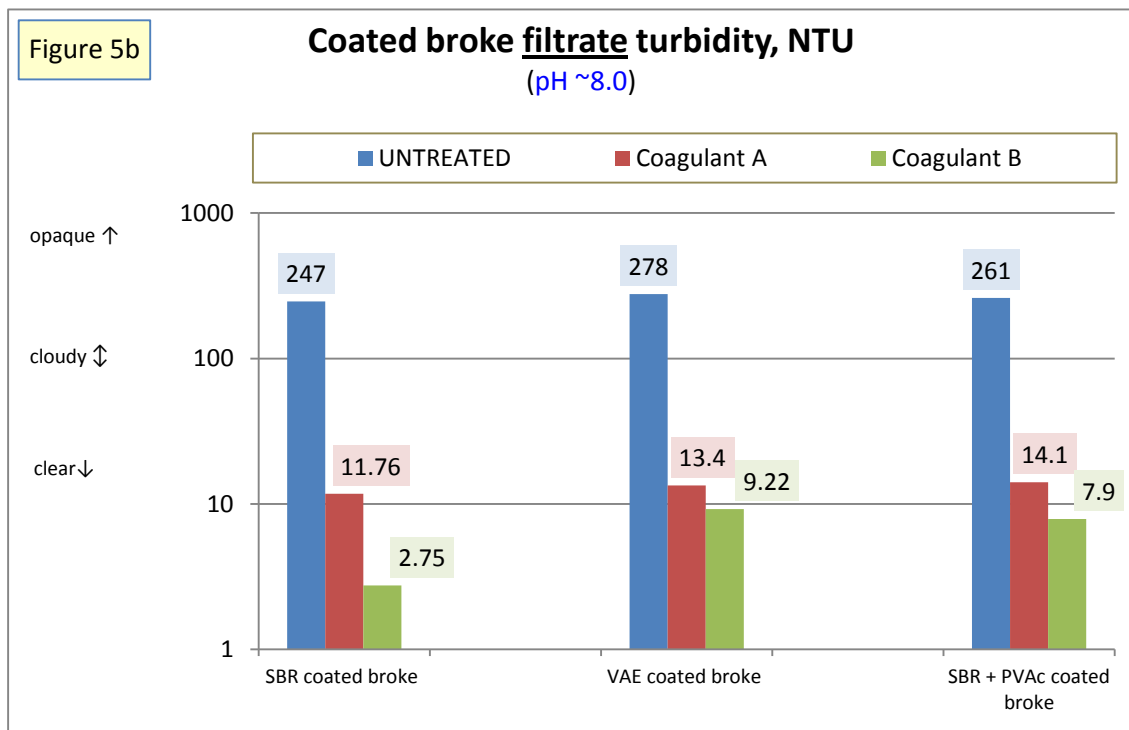
Figures 4a and 4b show the effects of each cationic coagulant on coated broke filtrate charge. Both dramatically reduced the starting anionic charges of all three coated broke. Note, however, that the resulting filtrate charge of all three treated coated broke under acidic conditions was cationic, suggesting that lower dosages of coagulant might be possible, and might be necessary, especially if an acid mill is employing other cationic chemicals at the wet ends of their paper machines. In both instances, Coagulant B (medium molecular weight, medium cationic charge, hybrid) appeared to be more efficient than Coagulant A (low molecular weight, high cationic charge). Regardless, both were able to effectively neutralize the higher anionic charges associated with the untreated VAE and SB/PVAc containing coated broke.



Concurrently, the filtrates were measured for turbidity and these results can be found in Figures 5a and 5b. Recall from our earlier experiments that the turbidity of alkaline coated broke was significantly higher than the turbidity of acidic broke. Additionally, the starting turbidities of all three untreated coated brokes (SB, VAE, and SB/PVAc blend) were about the same regardless of papermaking pH.

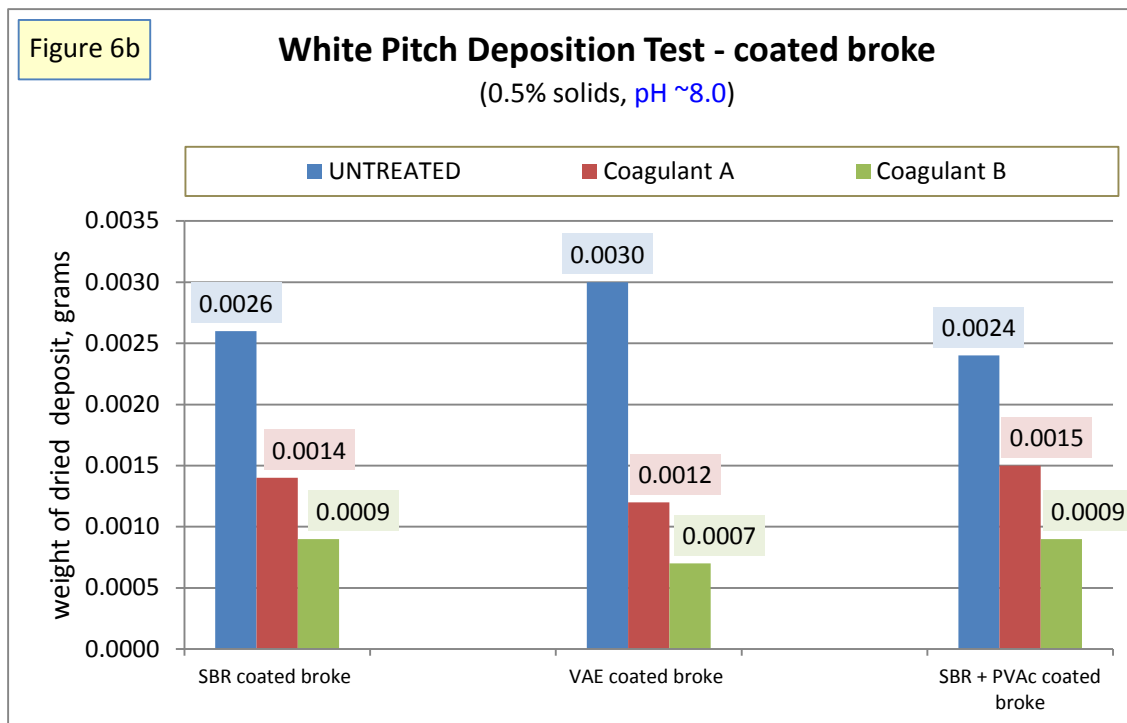
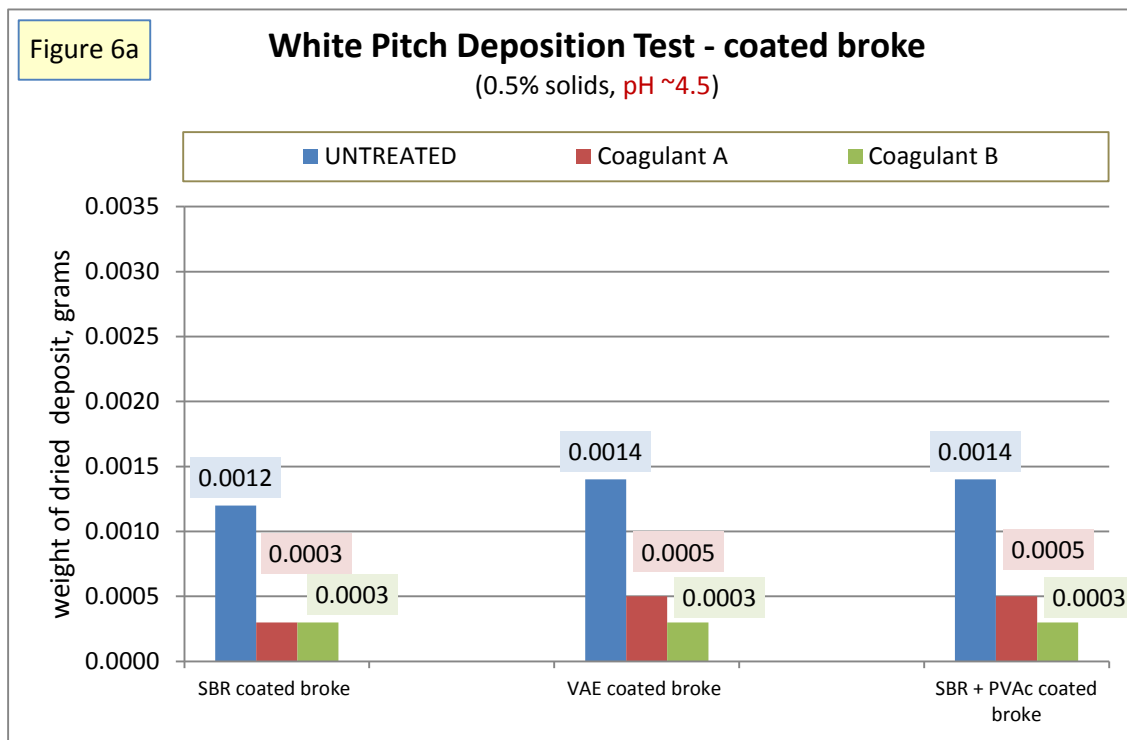
In this study, the addition of coagulant dramatically reduced the turbidity of the treated coated broke filtrates, strongly suggesting that these polymers fixed (bonded) the problematic white pitch components to the fibers, thus limiting their tendency to form deposits. Here, too, Coagulant B (medium molecular weight, medium cationic charge, hybrid) was more efficient than Coagulant A (low molecular weight, high cationic charge). In considering the positive impact of both coagulants, it might be possible to reduce their dosage and as result, their cost in use.





Lastly, we tested the treated brokes for their propensity to form troublesome deposits via the NC State white pitch deposition test.

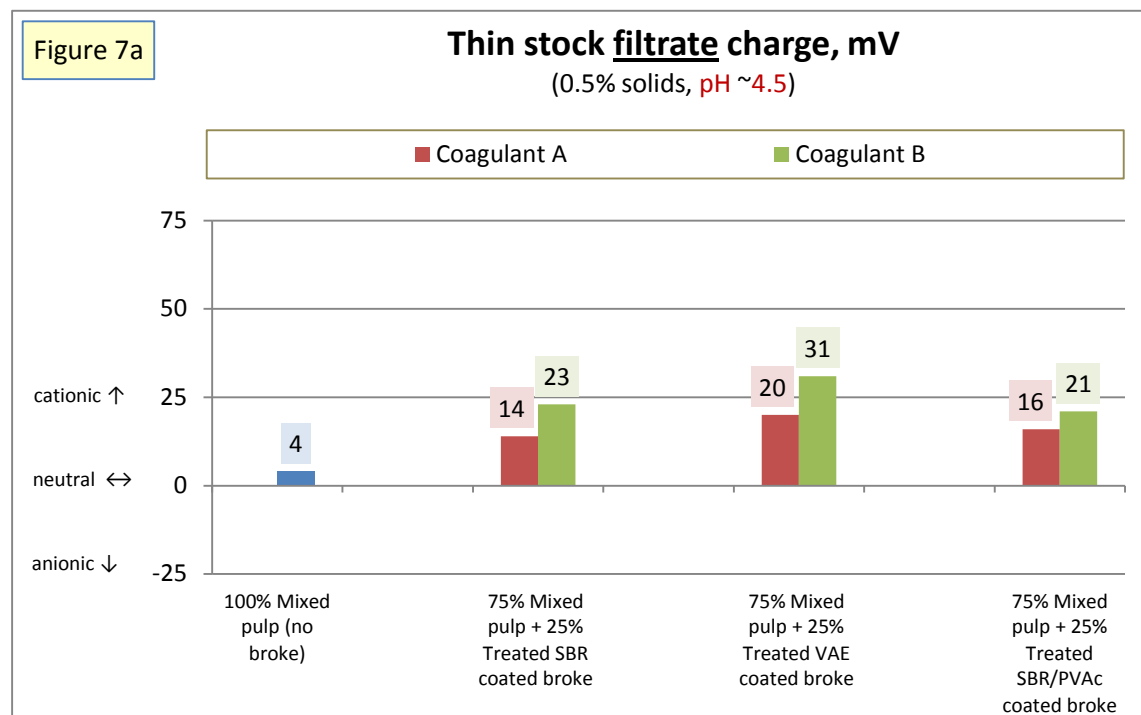
Figures 6a and 6b show the results of this deposition test. It was evident from the data that the treated coated brokes generated fewer deposits than the untreated coated brokes and that Coagulant B was more effective at reducing the amount of deposition than Coagulant A.

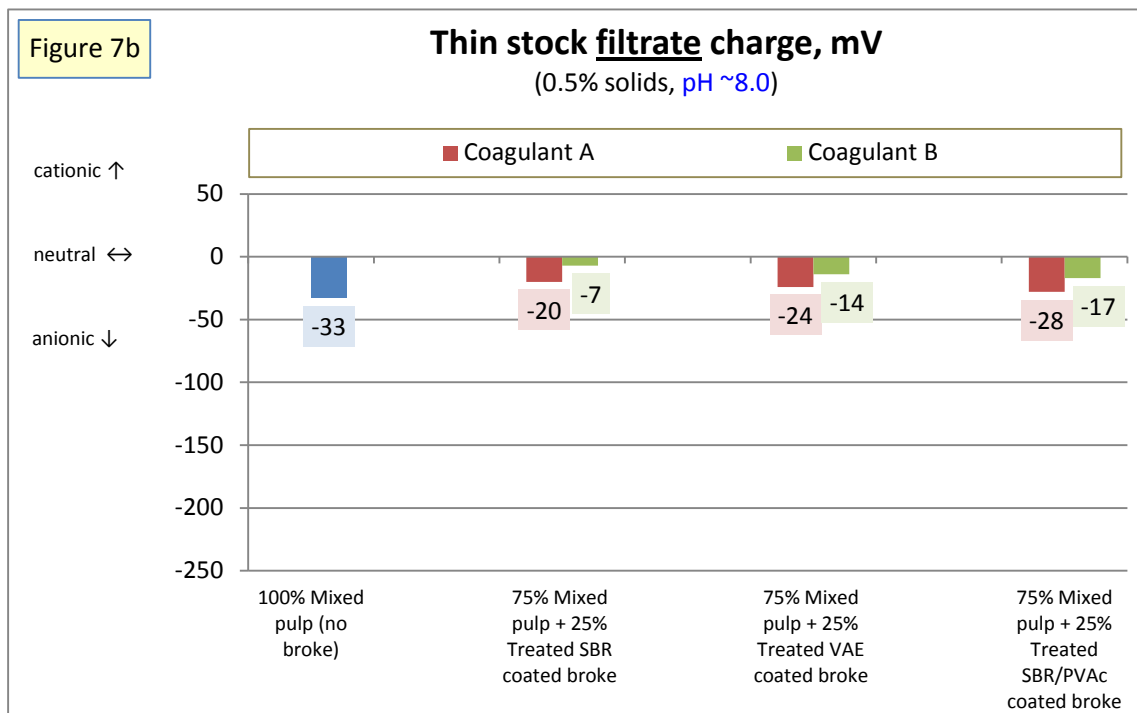


Having establishing the preceding profile for each coated substrate, we examined the effectiveness of each treatment further downstream in the wet end process namely the thin stock. In this study, each coated broke treated with each coagulant was blended with the mixed pulp fibers at ratio of 25/75 (o.d. basis) and tested the same way.

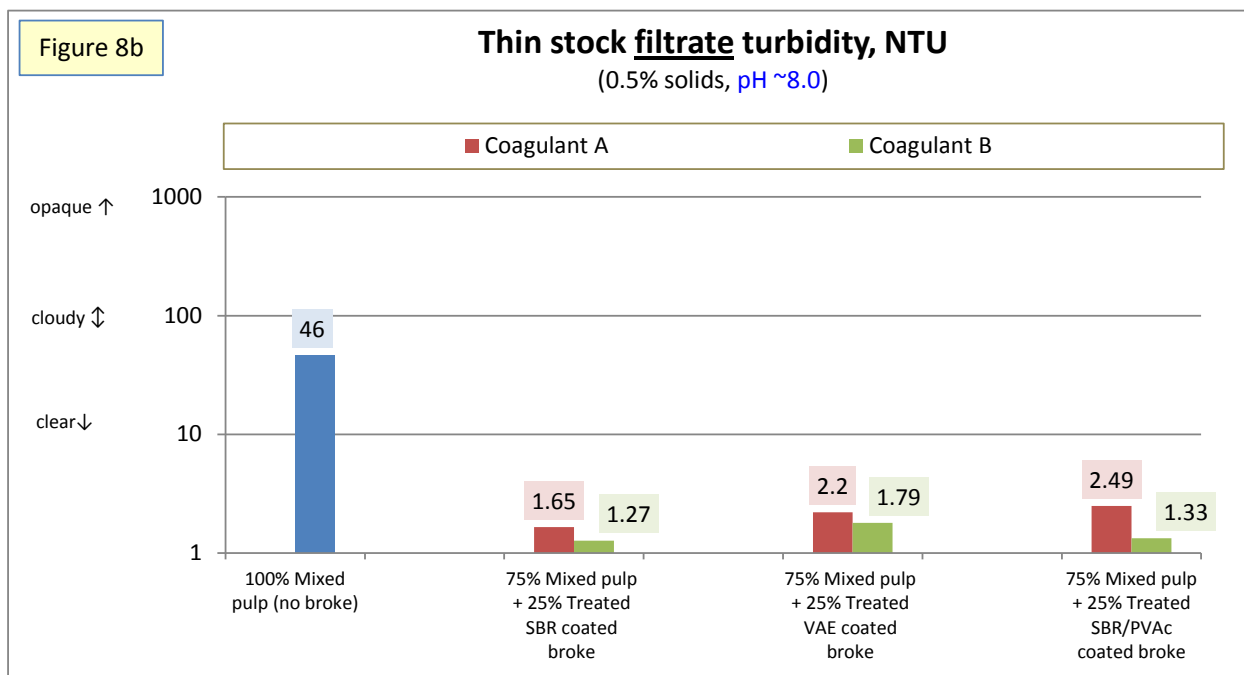
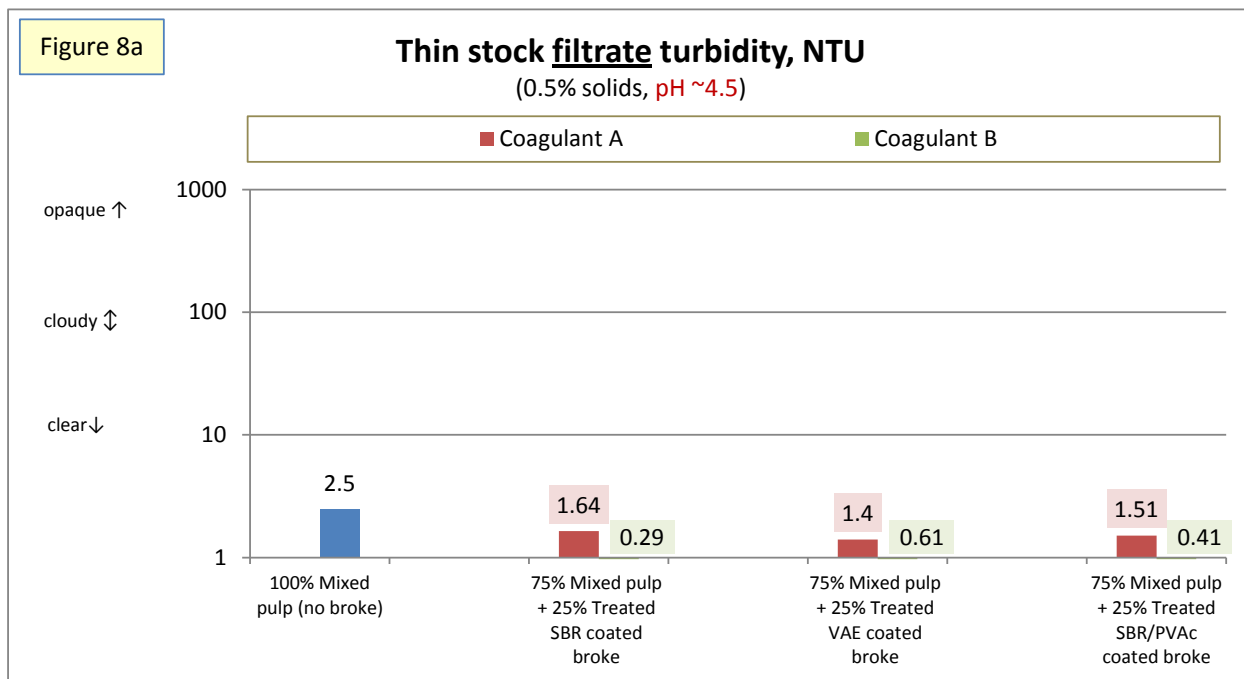
The charge results are shown in Figures 7a and 7b. All three acidic furnishes comprising treated broke were more positively charged than the broke-free pulp, once again, suggesting that the level of coagulant could be optimized if the goal is neutrality. More importantly, both coagulants helped close the original gap that existed between the SB containing coated broke and the two vinyl acetate-based systems (VAE and SB/PVAc blend).

Lastly, the anionic charge of the alkaline furnishes comprising treated broke was lower than the starting mixed pulp which again suggested that the treatment dosage could be lowered in order to balance the system charge. Plainly, both coagulants helped neutralize the anionic solubles and insolubles associated with the vinyl acetate binders thus making them less troublesome in this regard.





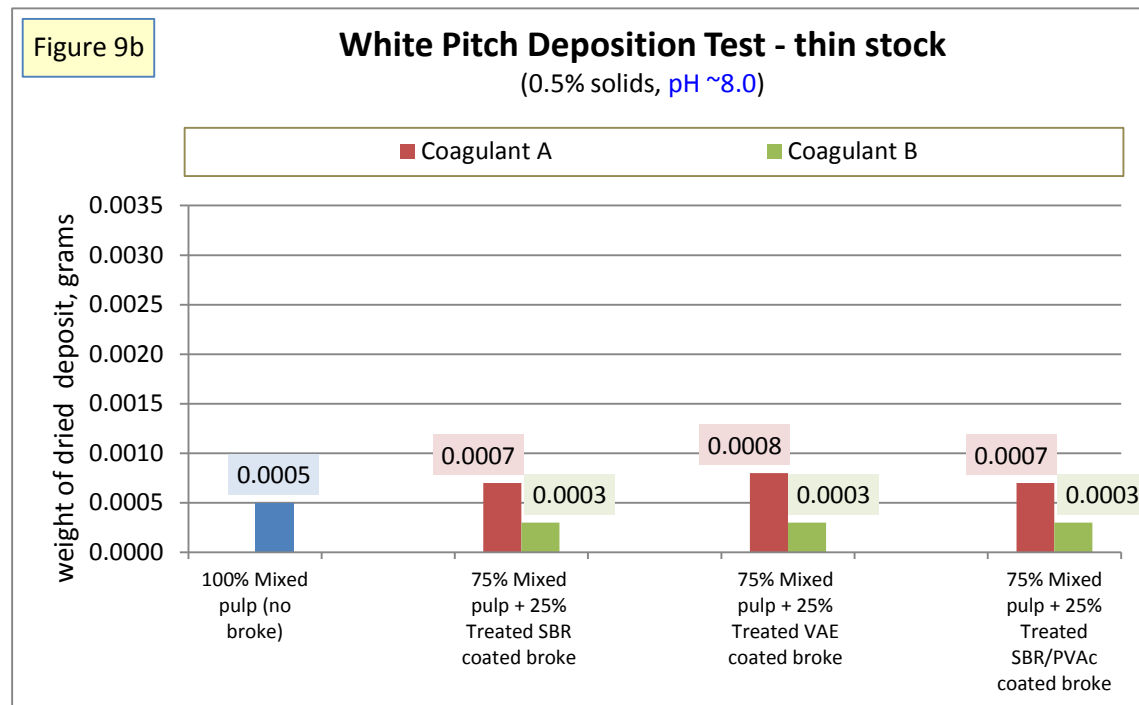
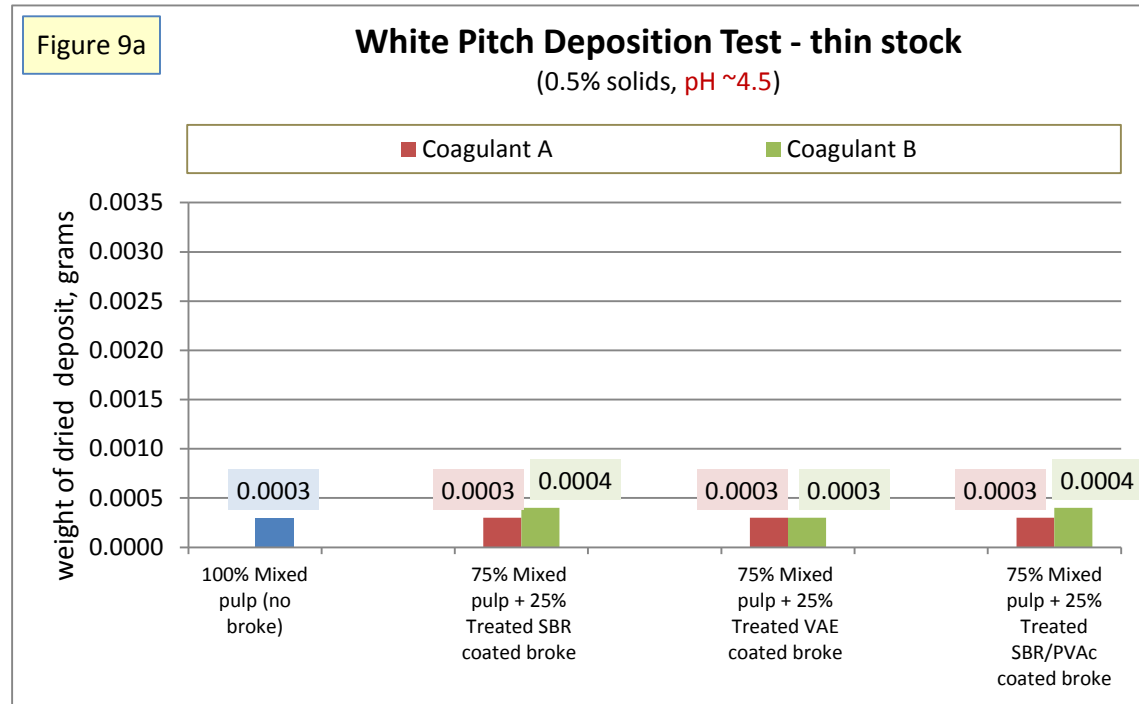
Figures 8a and 8b illustrate the effectiveness of both white pitch coagulants on the turbidities of the treated thin stock filtrates. Apparently, these polymers helped the pulp fibers fix and retain the troublesome coating particulates that came in with the coated broke regardless of papermaking pH and regardless of the synthetic binder. More specifically, there was no significant difference between SB, VAE, or the SB/PVAc blend. In fact, the filtrates of the furnishes comprising the treated coated brokes appeared to be clearer (less turbid) than the mixed pulp without any broke thus validating our contention that coagulant dosage can be reduced.



Finally, all the thin stock samples comprising mixed pulp and the treated coated brokes were subjected to high shear in the deposit test. The data obtained in this portion of the study can be found in Fig 9a and 9b. Shear did not generate any additional deposits in any of the thin stock systems confirming the effectiveness of each white pitch coagulant.

Under acidic conditions, the deposition weights of the mixtures comprising treated coated broke were comparable to the deposition weights of the mixed pulp without any coated broke.

Under alkaline conditions, Coagulant B appeared to be more effective than Coagulant A for white pitch control but the difference between SB, VAE and the SB /PVAc was virtually indistinguishable.



CONCLUSION

Vinyl acetate-based paper coating binders like VAE and PVAc have certain advantages and disadvantages when compared with its Styrenic counterparts. Its advantages can help papermakers immediately reduce their coating binder spend, resolve a quality deficiency and/or answer an unmet need. Its disadvantages can usually be overcome via coating reformulation and PVAc's reemergence as a good optimizer (i.e., partial substitution) and VAE's rise as a complete replacement for SB and SA latexes in coated paper applications is a testament to the determination of those spirited papermakers that are "in it to win it" in this seemingly declining industry.

Vinyl acetate's past history as a contributor to white pitch problems, unfortunately, has left an unforgettable bad taste in the mouths of many gray-beards and for this reason, many paper mills still have not taken advantage of the potential benefits of this binder technology. One underlying purpose of this paper, therefore, is to educate and hopefully chase away some of the demons that have plagued said papermakers for many decades because it is this author's opinion (a fellow gray-beard that's lived through many outbreaks of white pitch on numerous machines) that several factors other than the type and amount of PVAc could have influenced said issues in the past. Recall the trials and tribulations associated with transitions from acid to alkaline papermaking and the ensuing changes in wet end and coating chemistry that occurred many years ago, as one example.

All commonly used synthetic binders can have a major impact on white pitch⁹. One reason why some vinyl acetates behave the way they do is because they are more anionic than some SB or SA latexes. As such, coated broke comprising vinyl acetate-based binders can affect the charge of a wet end depending on how much is introduced to a particular furnish. Further, PVAc is more hydrophilic and therefore more water-soluble than SB. With time and shear, it can generate a higher quantity of particulates and solubles in the coated broke (i.e., turbidity) than the more hydrophobic VAE and Styrenic binders. This attribute, coupled with its negative charge, can contribute to the anionic trash content of a wet end and as a consequence tie up or deactivate other additives required for good sheet formation, runnability, and surface quality.

Today, the paper industry has new technology that it can use to overcome just about any problem including white pitch. Turbidity and charge analysis, for example, are useful testing and measuring methods that can help predict and therefore, enable corrective actions that will curb white pitch problems on a machine. Cationic coagulants, in particular, can effectively neutralize the troublesome anionic charges associated with some vinyl acetate-based coating binders and reduce the number of particulates they generate in the coated broke tank by firmly anchoring them to the fibers.

Understanding the nature and behavior of a synthetic coating binder can help papermakers, suppliers, and academia measure and therefore predict how it will interact in the wet end of a paper machine once it reaches there via the coated broke. Matching binder chemistry with the proper treatment program should alleviate white pitch problems and give coated paper producers more confidence to explore the potential benefits of vinyl acetate-based coating binders going forward.

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- Rick Cazenave at Celanese Emulsions.
- Martin Hubbe, Richard Venditti, and Matthew Kollman at NC State University, Dept. of Wood and Paper Science.
- Ross Gray and Michael Ancona at Nalco Company.
- Craig Mitchell at Ashland.