

# **Peracetate Singlet Oxygen Chemistry as a Safe, Simple and Effective Alternative for Peracetic Acid**

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## **ABSTRACT**

The use of singlet oxygen chemistry for a variety of applications in pulp and paper production shows exciting potential for technical performance, supply logistics, safety and cost. Recently developed technology to provide singlet oxygen chemistry in a liquid peracetate concentrate has shown many performance similarities to peracetic acid (PAA), which has been extensively studied and used in pulp and paper mills. Distilled PAA (dPAA) was developed to provide an industrially practical formulation of PAA at mill scale. Its use was originally motivated by TCF bleaching and then developed to enhance ECF bleaching and papermaking as the industry shifted focus. However, the use of dPAA has been severely challenged by logistical and capex hurdles associated with supplying mills. The singlet oxygen chemical technology, with a similar chemical profile, shows potential to provide comparable or better technical performance to PAA while eliminating the logistics, safety and cost hurdles of providing dPAA.

The singlet oxygen chemistry, like dPAA, has the potential to, provide post-bleach brightening/whitening and increase color stability. The singlet oxygen chemistry can also provide a variety of benefits in the paper mill such as microbial control, odor control and enhanced OBA response. Laboratory studies presented demonstrate how the proven mill-scale benefits of dPAA can be realized by a similar yet more easily deployable chemistry.

## **INTRODUCTION**

Peracetic acid (PAA) is an established, but infrequently utilized bleaching chemistry for kraft pulp. Distilled peracetic acid (dPAA) is in commercial use today to delignify pulp for lowering the kappa number; brighten pulp to increase brightness/whiteness; and inhibit color reversion. The chemical production, storage and handling requirements of dPAA, which require significant capital investment, has limited its global commercial success with only a few mills using it in a concentrated geographic area.

Peracetic acid (PAA) has been shown to be particularly attractive in treating bleached kraft pulp. It can be easily added in existing storage chests or in the stock preparation chests. Small charges such as 2-3 lbs PAA per ton can increase 88 ISO brightness kraft pulp by 1.5 to 2.5 points. Charges of 7 lbs per ton or more increase brightness marginally. It produces whiter pulp with less yellowing (lower b value) and importantly improves brightness stability by reducing reversion. Reduced reversion can thereby facilitate less need for overbleaching in order to guarantee target specifications. At typical charges there is minimal reaction between PAA and optical brightening agents; furthermore, PAA may reduce or obviate the need for OBAs. Small residual presence of PAA eliminates microbes in the paper machine white water system and reduces biofilm deposits. Post-bleaching PAA treatment has been shown to improve dewatering at the drying machine. Lastly, PAA is biodegradable with no toxic by-products; it decomposes to acetic acid, water, and oxygen<sup>1,2,3</sup>.

Peracetate-based singlet oxygen chemistry, a recently patented technology, is a very similar chemistry to PAA. It was anticipated that sodium peracetate (NaPAc), a commercially manageable form of peracetate,

could deliver similar benefits for kraft pulp treatment as dPAA but without the practical complications. This project was modeled after a body of work conducted to demonstrate PAA performance. Initial results confirm that peracetate-based singlet oxygen chemistry can indeed deliver similar and potentially better performance relative to PAA and ClO<sub>2</sub>. This paper will provide a brief overview of the singlet oxygen chemistry and recent results examining its performance for post-bleaching brightening and inhibition of color reversion.

Peracetate-based singlet oxygen chemistry is safely produced on site as a formulated sodium peracetate solution using chemicals normally found at paper mills plus an additional non-toxic, safe to handle ingredient. The equipment used for generating and dispensing the peracetate product is a low power, low pressure, automated system of metering pumps and an in-line reactor process contained in a relatively small footprint. The capital and operating costs of such equipment is minimal compared to that of a ClO<sub>2</sub> plant or distilled PAA plant. With a small footprint it can be easily retrofitted into a facility.

The use of molecular oxygen in its “singlet” excited electronic state has several attractive qualities as a pulp bleaching and/or delignification agent. “Singlet oxygen,” <sup>1</sup>O<sub>2</sub> (<sup>1</sup>Δ<sub>g</sub>), as it is often referred to, is highly reactive towards lignin and other electron-rich materials while being virtually unreactive toward cellulosic fiber. Efforts in the 1980’s and 1990’s were made to investigate singlet oxygen’s potential for pulp brightening. However, available methods for generating singlet oxygen on the scale of mill processes have been impractical, low yield and cost prohibitive.

Molecular oxygen in the atmosphere is in its ground state electronic configuration, which is a triplet spin state, designated as <sup>3</sup>O<sub>2</sub> (<sup>3</sup>Σ<sub>g</sub><sup>-</sup>), representing the two unpaired electrons in the highest occupied molecular orbitals. The first excited state finds the two electrons paired within the two degenerate orbitals in the singlet oxygen state, <sup>1</sup>O<sub>2</sub> (<sup>1</sup>Δ<sub>g</sub>) with lifetimes on the order of several microseconds in water to several hundred microseconds in aprotic solvents. The second, higher energy excited state is also a singlet state (<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) with the spin-paired electrons in different orbitals. Its lifetime is extremely short and decays to the <sup>1</sup>Δ<sub>g</sub> state before chemical reactions can occur. Triplet oxygen is a di-radical while singlet oxygen configurations are non-radical states.

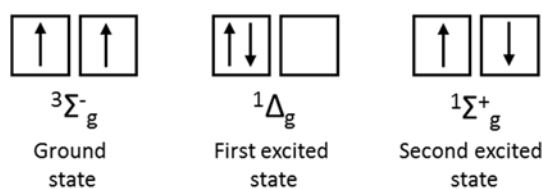


Figure 1. Representation of electronic states of molecular oxygen.

The electronic configuration of singlet oxygen allows it to undergo a variety of reactions including formation of endoperoxides, formation of allyl peroxides by Alder-ene reactions, formation of 1,2-dioxetanes, reactions with phenols, reactions with sulfides, and reactions with primary and secondary amines<sup>4,5</sup>.

There are several known methods to generate singlet oxygen in solution for chemical reactions such as photo-chemical excitation of triplet oxygen<sup>6,7</sup> (e.g., ultraviolet light radiation, microwave radiation, photochemical dye-sensitized energy transfer) and chemical generation pathways<sup>8,9</sup> (e.g., hydrogen peroxide reaction with hypochlorite, decomposition of Caro’s acid catalyzed with ketones<sup>10</sup>, reaction of ozone with aryl phosphates, decomposition of peracetic acid). Photochemical methods generate low

concentrations of singlet oxygen localized near a radiation source and are not practical for optically opaque environments such as pulp. Chemical methods are generally suitable in the laboratory, but are expensive, require specific reaction conditions (not compatible with other processes), often have undesirable or toxic byproducts, and are not efficient or practical for large scale applications.

A patented chemical technology recently developed by Clean Chemistry, Inc. to generate singlet oxygen and related reactive oxygen species (ROS) has overcome the limitations of scaleup, efficiency and process compatibility. The ROS technology rapidly generates a liquid “parent” oxidant solution specially formulated to efficiently produce singlet oxygen in-situ by the decomposition of sodium peracetate. The product is free of chloride and sulfate and the byproducts are glycerin and sodium acetate. The technology is inherently safer, less corrosive and has very low AOX formation potential relative to chlorine and chlorine dioxide<sup>11</sup>. Earlier results show a high level of activity and selectivity for reactions of singlet oxygen with lignin (i.e., kappa reduction) and brightening in hardwood and softwood pulps<sup>8</sup>. This technology was successfully scaled up for industrial applications and has been used for oilfield water treatment and reuse since 2014. More recently the technology was demonstrated in a paper mill trial for repulping paper treated with wet strength binders.

Results of this study demonstrated that the performance of peracetate-based singlet oxygen chemistry is at least equivalent to PAA for brightening and color stability and that the major differences between these chemistries are not performance, but safety, handling and capital costs.

## **METHODS**

Bag bleaching tests conducted at 5% and 10% pulp consistency, 60° C, 2 hours. The pH was adjusted with 1 N H<sub>2</sub>SO<sub>4</sub> or 1 N NaOH to achieve a final pH of 5, 7 or 9. Samples were heated in a heated water bath and kneaded every 10-15 minutes. Samples were washed twice with distilled water and filtered with a Buchner funnel. The washed fiber was divided into two equal portions (by weight) to make two brightness pads (6 g dry fiber per pad).

Brightness pads were prepared by the method described in Section 8 of T218 (Buchner funnel procedure). Brightness pads were dried in drying rings overnight with air flow from a fan. Air temperature 21-23° C, relative humidity 26-34%. D65 Brightness and L-a-b measurements were made using a Colortouch model ISO brightness meter. Four measurements on each sample were averaged.

Reversion test procedure using TAPPI Method T544 at 90°C, 50%, relative humidity with sampling times of 4, 8, and 24 hours.

## **RESULTS**

The primary performance comparison was made between PAA and sodium peracetate (NaPAC) at three different pH levels, which impact the rate of singlet oxygen production and NaPAC:PAA ratio. A commercial grade of equilibrium ePAA (17% wt/vol) was used in the brightening tests and its concentration measured prior to use. It was demonstrated previously that the brightening performance of ePAA and dPAA is the same<sup>3</sup>. Chlorine dioxide was prepared as a 0.3% solution and its concentration measured prior to use.

Brightening tests were conducted on hardwood pulp collected from a fiber line after a D-O-D bleach sequence. The pulp had an initial pH of 6.5-7.0 and 14.2% consistency. Bag bleaching tests at 5% and

10% consistency were conducted at 60°C for 2 hours with the nominal final pH listed for each oxidant for the brightness curves in Figures 2 and 3.

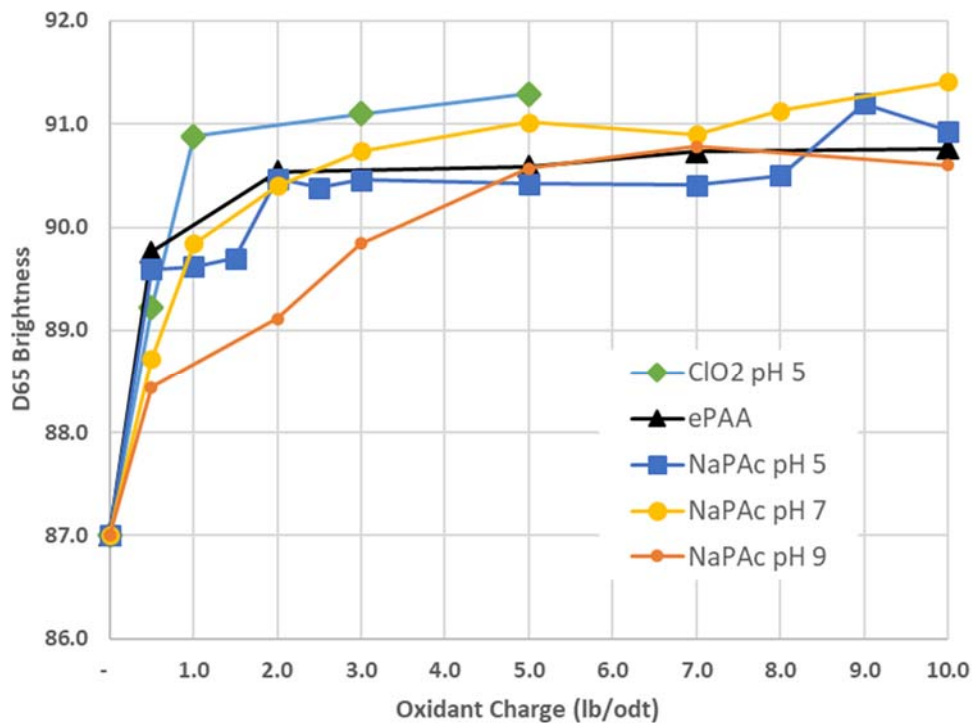


Figure 2. Brightness curves at 5% consistency.

At 5% consistency the brightness gains up to about 3 lb/odt oxidant charge are very similar for ePAA at pH 5, and NaPac at pH 5 and 7. The pH 7 NaPac treatment provides a modest brightness gain as oxidant charge continues to increase. The NaPac at pH 9 provides less brightening at 5% consistency until higher concentrations. Chlorine dioxide provides a rapid brightness gain at 1 lb/odt, but does not provide significant gains above that chemical charge. The pH 5 ePAA and NaPac treatments do not significantly increase in brightness above 3 lb/odt.

At 10% consistency, Figure 3, the brightening performance of all oxidants and pH conditions is very similar up to about 5 lb/odt oxidant charge. The pH 9 NaPac brightening is greater at higher consistency due to the shorter diffusion path through the liquid phase that singlet oxygen (produced in the liquid phase) needs to travel before reacting with the fiber. Singlet oxygen has only a few microseconds lifetime in water to diffuse and react before it relaxes back to the ground state (triplet oxygen).

The ClO<sub>2</sub> brightness gains at 10% consistency are lower than observed at 5% consistency. This repeatable behavior is likely due to more rapid off-gassing of ClO<sub>2</sub> at higher solution concentrations during addition to the pulp in laboratory conditions. Comparatively, sodium peracetate NaPac is a low volatility, low odor, safe and easy to use chemistry.

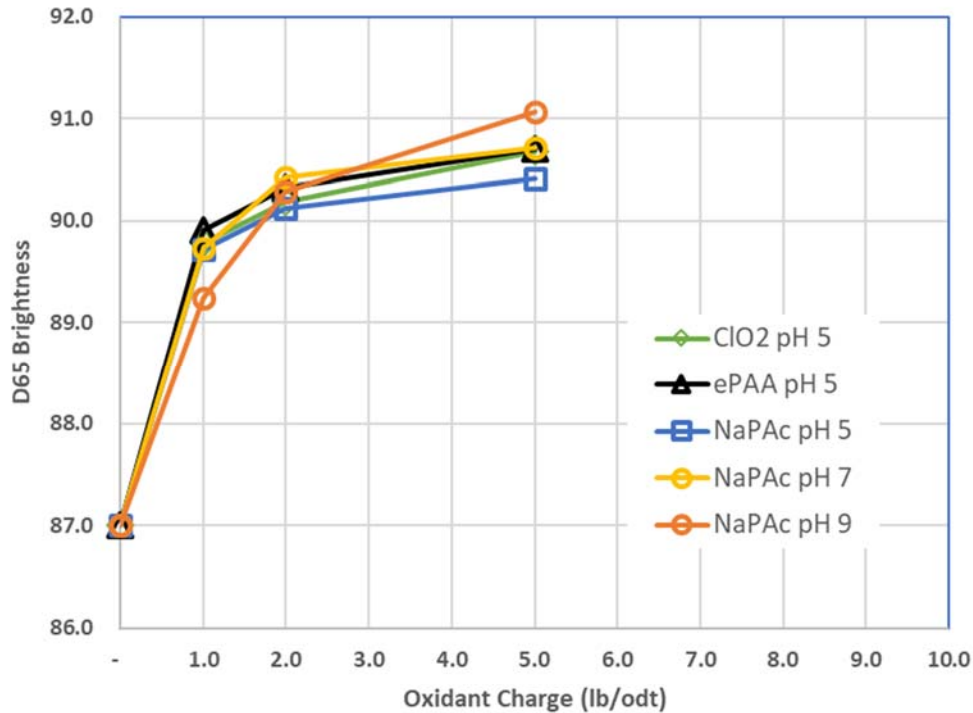


Figure 3. Brightness curves at 10% consistency.

Brightness pads were tested for color reversion using the standard TAPPI method T544. D65 brightness measurements were made at 0, 4, 8 and 24 hours of exposure to test conditions. The reversion results at 1 lb/odt and 5 lb/odt oxidant charges are shown in Figures 4 and 5, respectively.

After brightening pulp with 1 lb/odt oxidant charge, Figure 4, the rate of reversion was greatest for  $\text{ClO}_2$ , especially at the shorter time intervals. Reversion rates for ePAA at pH 5 was slightly greater than for NaPAC at pH 5, which should reflect the very similar peracid forms present at that pH. Reversion rates were slower at pH 7 and slower again at pH 9 for NaPAC, especially at the longer time intervals. As pH rises the rate of singlet oxygen species generated from NaPAC increases making this chemistry uniquely effective at higher pH levels.

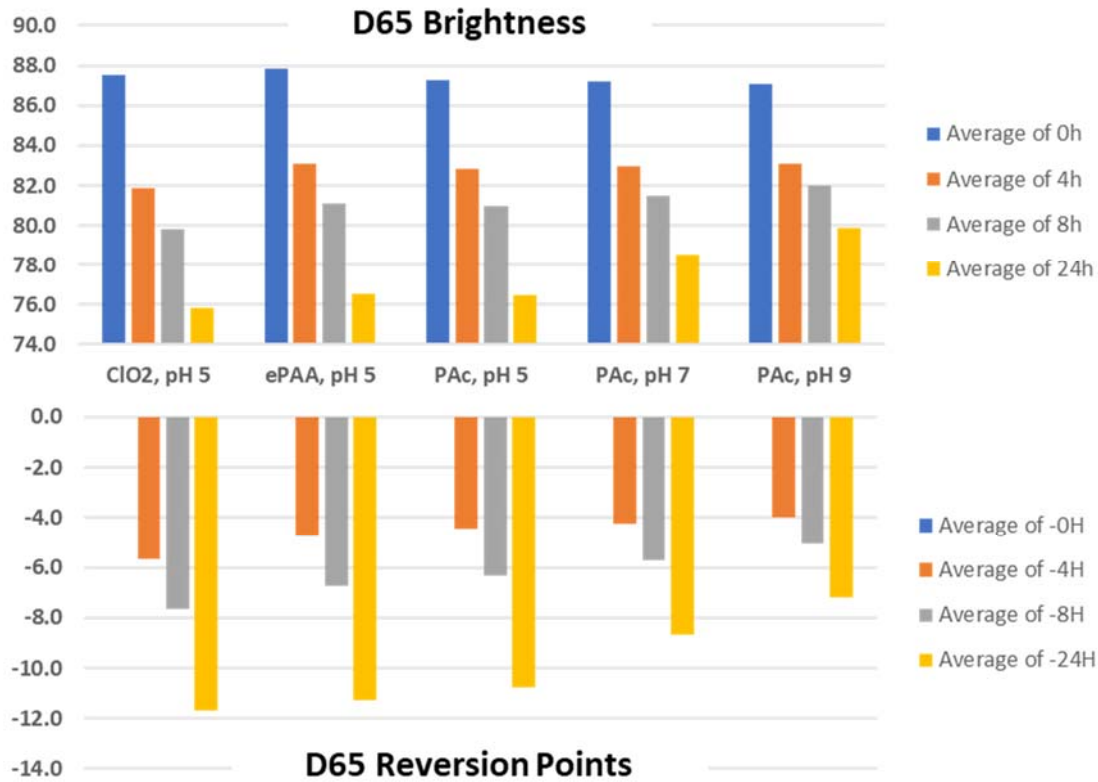


Figure 4. Reversion test results for pulp brightened with 1 lb/odt oxidant charge. Measured D65 brightness over time (upper panel) and D65 reversion from initial, 0 hours (lower panel).

The above trends are nearly the same after brightening pulp with 5 lb/odt oxidant charge in Figure 5. The total D65 points reversion is not significantly different between the 5 lb/odt and 1 lb/odt oxidant charges even though the initial brightness was greater at 5 lb/odt.

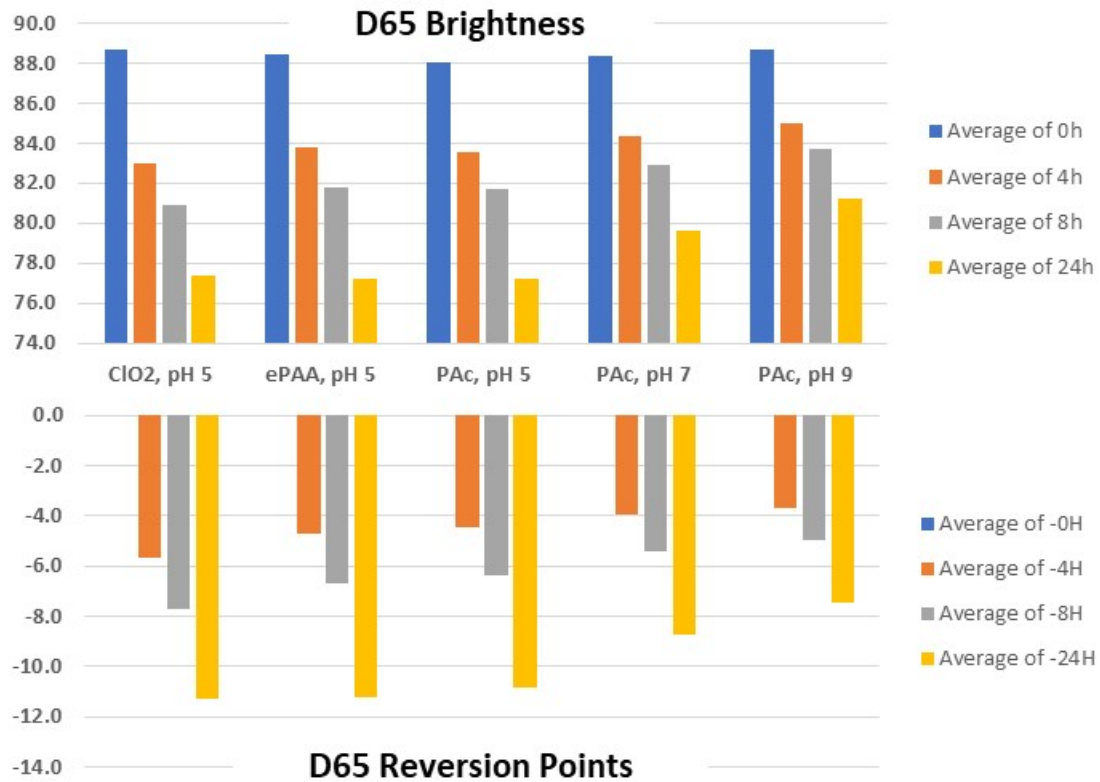


Figure 5. Reversion test results for pulp brightened with 5 lb/odt oxidant charge. Measured D65 brightness over time (upper panel) and D65 reversion from initial, 0 hours (lower panel).

The brightness pads were evaluated for changes in color. L a b was measured to compare whiteness and yellowing. Results for pulp brightened with 5 lb/odt oxidant charge are presented in Figure 6. The Untreated pulp (no oxidant charge) control had the lowest whiteness, L, and highest yellowing, b. The brightened pulp had increased L and decreased b, although the ePAA treated pulp was more yellow than the others. After 24 hours reversion, L decreased, and b increased. The ePAA treated pulp exhibited significantly greater yellowing than the others. The pH 9 NaPAC treated pulp had the least amount of yellowing, similar to ClO<sub>2</sub>.

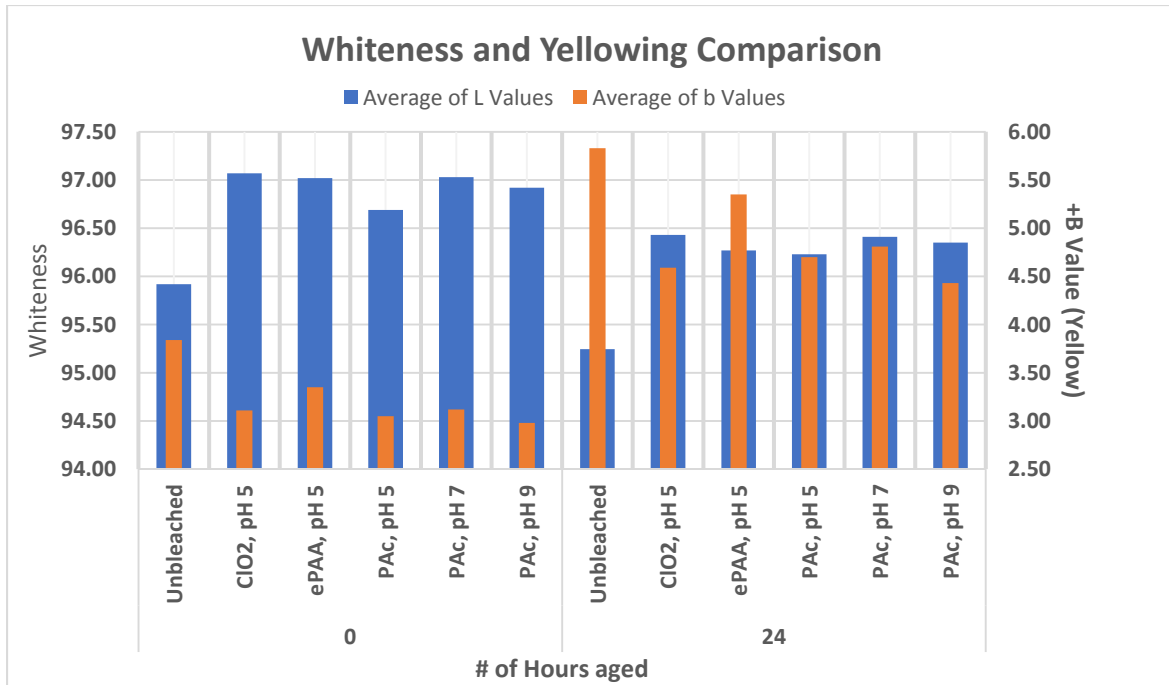


Figure 6. Whiteness and yellowing comparison for pulp brightened with 5 lb/odt oxidant charge at 0 hours (left side) and 24 hours (right side). Untreated control samples were included for comparison.

As for other beneficial uses in a paper mill, the peracetate-based singlet oxygen chemistry is well suited for microbial control, which is accelerated at elevated temperatures. In general, the production of singlet oxygen greatly enhances microbial control compared to PAA such that significantly less chemistry is needed to provide effective treatment. The example in Figure 7 illustrates the difference in performance between the peracetate chemistry and ePAA commonly used in water treatment. The test challenge was produced water from oilfield production operations. The water contained suspended solids, iron, high total dissolved solids and moderately high microbial activity.

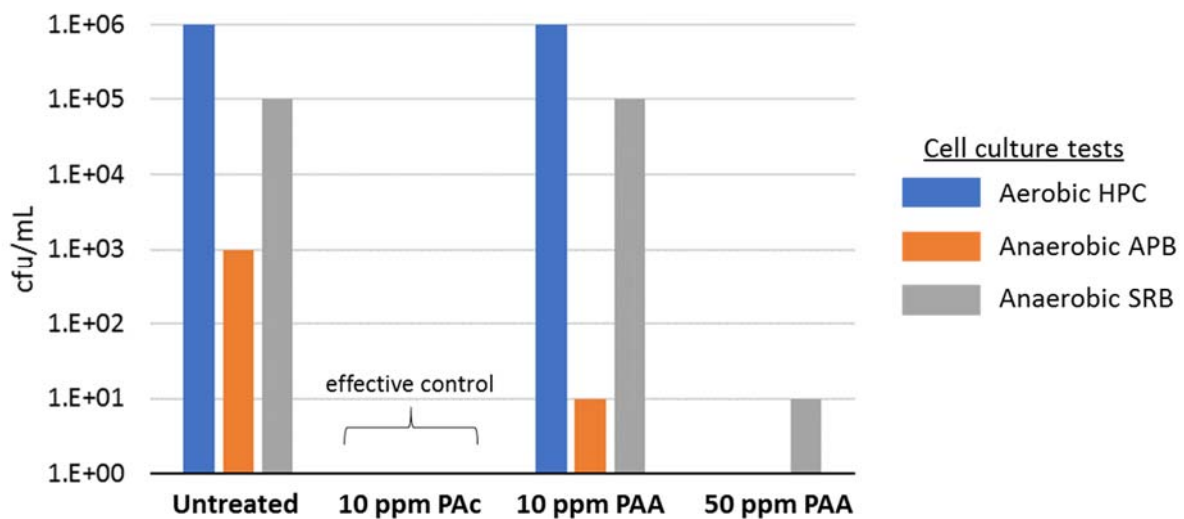




Figure 7. Comparison of microbial activity in oilfield produced water treated with 10 ppm peracetate-singlet oxygen chemistry (PAC) versus 10 ppm and 50 ppm PAA. Three categories of microbes were measured: HPC = heterotrophic plate counts; APB = acid producing bacteria; SRB = sulfate reducing bacteria.

The produced water was treated with oxidant and then tested for microbial activity 12 hours later to demonstrate that microbial control was achieved rather than temporary inhibition of growth. At least 5 times the active PAA concentration was needed in this water for adequate microbial control.

## CONCLUSIONS

Peracetic acid has several potential strengths as an oxidizing chemistry on kraft pulp. Practical commercial considerations have prevented widespread usage. The performance of peracetate singlet oxygen chemistry was comparable to PAA for post-bleaching brightening regarding whitening pulp, improving brightness stability, and reducing yellowing. Importantly, results indicate that the presence of singlet oxygen produced by the peracetate chemistry can provide better performance for preventing reversion and yellowing. This performance can be achieved over the wide range of pH values typically found in pulp storage chests with near-neutral to slightly alkaline conditions being preferred. The peracetate singlet oxygen chemistry can be easily added in existing HD storage chests or in the stock preparation chests, is compatible with mill equipment and is inherently safe to use. Peracetate singlet oxygen chemistry is produced on site in a simple apparatus and avoids the high capital investment hurdles of chemical production, storage, and handling requirements presented by dPAA.

## REFERENCES

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Gateway to  
the Future



# Peracetate Singlet Oxygen Chemistry as a Safe and Simple Alternative for Peracetic Acid

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# Project Background and Summary

- Peracetic acid (PAA) has been demonstrated as a commercially viable bleaching chemistry for kraft pulp; this chemistry is in commercial use today to
  - Delignify pulp to lowering the kappa number
  - Brighten pulp to increase brightness/whiteness
- Chemical handling requirements driving capital investment has limited PAA's global commercial success with only a few mills using it in a concentrated geographic area
- Na Peracetate Singlet Oxygen Chemistry, a recent patented technology, is a very similar chemistry to PAA; it was expected that it could deliver the same benefits for kraft treatment as PAA but without cumbersome handling considerations
- This project followed brightening work done for PAA and initial results confirm that Na Peracetate can indeed deliver similar performance to PAA and ClO<sub>2</sub> without the main drawbacks.
- Na Peracetate is safely produced on site using chemicals normally found at paper mills plus an additional non-toxic, safe to handle ingredient. Only a modest make-down system is required.

# Presentation Outline

- **Clean Chemistry Overview**
- Benefits of Peracetic Acid (PAA) for Treating Kraft Pulp
- Peracetate Singlet Oxygen Chemistry versus PAA
- Brightening and Reversion Results
- Conclusions

# Clean Chemistry, Inc. Background

- Formed in 2014 to commercialize a new oxidation chemistry
- Core technology for large-scale production and application of **singlet oxygen chemistry generated from sodium peracetate**
- Holds patents for a novel chemistry, production methods, and its uses
- Commercial application started in oilfield water treatment and reuse; now widely accepted as viable alternative to  $\text{ClO}_2$
- Less corrosive alternative in many applications where chlorine chemistries are historically used, e.g., cooling tower water treatment

# Novel Oxidation Chemistry

- The Na Peracetate singlet oxygen chemistry is a patented oxidant technology designed to deliver large quantities of reactive oxygen species (ROS) in a liquid solution
  - Singlet oxygen,  $^1\text{O}_2$  (primary ROS)
  - Superoxide,  $\text{O}_2^{\cdot-}$
  - Hydroperoxyl radical,  $\text{HOO}^{\cdot}$
- Solution is mildly alkaline with low volatility
- Mild odor (weak vinegar)
- Non-persistent; reacts rapidly; must be used shortly after on-site generation
- Residuals are biodegradable and GRAS
- Na Peracetate chemistry is TSCA listed and an EPA registered biocide for industrial uses

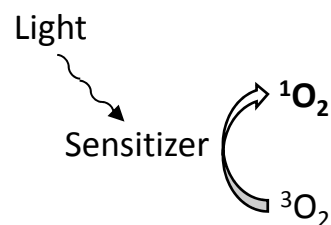
# What Is Singlet Oxygen Chemistry?

## Characteristics

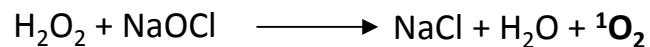
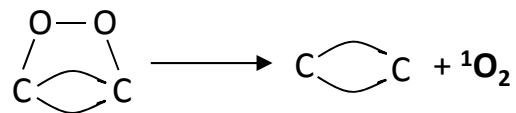
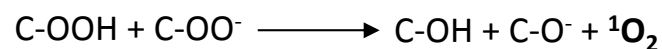
- Molecular oxygen in its electronically excited state
- Short lifetime in water - microseconds
- Selective reactivity with electron-rich materials (substituted aromatics, olefins)
- Particularly reactive with lignin and phenolic materials
- Can be produced from chemical precursors/carriers

## Production Methods

### Photolysis



### Chemical Pathways





# Background to Industrial Uses of Singlet Oxygen Chemistry

## **EXAMPLES OF USES**

- Historic use in chemical research
- Laboratory investigations for photodynamic therapy of tissue and blood sterilization
- Historic patents filed for pulp bleaching and microbial control

## **BARRIERS TO COMMERCIALIZATION**

- Short shelf life requires on-site generation
- Ultraviolet light or photosensitized dye systems typically required
- Large-scale, efficient production by chemical methods not previously developed

**Overcoming technical barriers of large-scale generation on-site through a chemical process has created new opportunities for industrial uses of under-utilized ROS**

# New Chemical Generation of Singlet

## Oxygen



- Novel sodium peracetate solution production method optimizes singlet oxygen generation
- Chemistry is produced in compact, rugged process compatible with industrial environments
- Automated production equipment has built-in QC measures assuring consistent product performance
- System capacity readily scaled to serve industrial demand

# Industrial Benefits and Uses of Peracetate Singlet Oxygen Technology

## **Benefits**

- Inherently safer technology than most other industrial oxidants
- Selective oxidant is easier on equipment; less corrosive
- Effective over wide pH range
- Generated on-site, on-demand

## **Industrial uses**

- Industrial scale oxidant
- Bleaching/Brightening agent
- Microbial control
- Odor control - sulfide control
- Break oil emulsions
- Water clarification

# Presentation Outline

- Clean Chemistry Overview
- ➔ • **Benefits of Peracetic Acid (PAA) for Treating Kraft Pulp**
- Peracetate Singlet Oxygen Chemistry versus PAA
- Brightening and Reversion Results
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# Studied Benefits of Peracetic Acid (PAA) for Treating Kraft Pulp

- Peracetic acid (PAA) can be used to delignifying pulp to materially reduce kappa number
  - Used as a replacement for  $\text{ClO}_2$
  - Used to bleach TCF pulps
- ➔ • Peracetic acid (PAA) can be used to brighten pulp
- Improve pulp quality
- Reduce water usage
- Improve microbial control

# Documented Benefits of Peracetic Acid (PAA) for Brightening Kraft Pulp close to PMs

- Peracetic acid (PAA) can be added to bleached kraft in storage chests or in the stock preparation chests
- Small charges such as 2-3 lbs PAA per ton increases the brightness of 88 ISO bleached kraft pulp by ~1.5% to 2.5% ISO. Dosage of 7 lbs per ton or more increase brightness marginally
- Whiter pulp with less yellowing (Lower b value)
- Improves brightness stability. PAA limits brightness reversion resulting in less need for overbleaching
- At typical dosages there is minimal reaction between PAA and optical brightening agents, furthermore PAA may reduce or obviate the need for OBAs
- Small residual presence of PAA eliminates microbes in the paper machine white water system and reduces biofilm deposits
- Improves dewatering at the drying machine

# Obstacles to Widespread Use of PAA

- Due to supply economics peracetic acid is commercially delivered as distilled version (dPAA) which requires further investment in capital equipment for production
- dPAA plants must be reasonably close to mill sites for handling reasons, so the distribution radius is constrained
- Due to product stability issues, dPAA must be stored at refrigerated conditions. Handling considerations mandate capital investment for storage and handling equipment at the mill sites
- Handling requirements driving investment has limited PAA's global commercial success with few mills using it only in concentrated geographic areas

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# Comparison: Peracetate vs. Peracetic Acid

## How they are similar

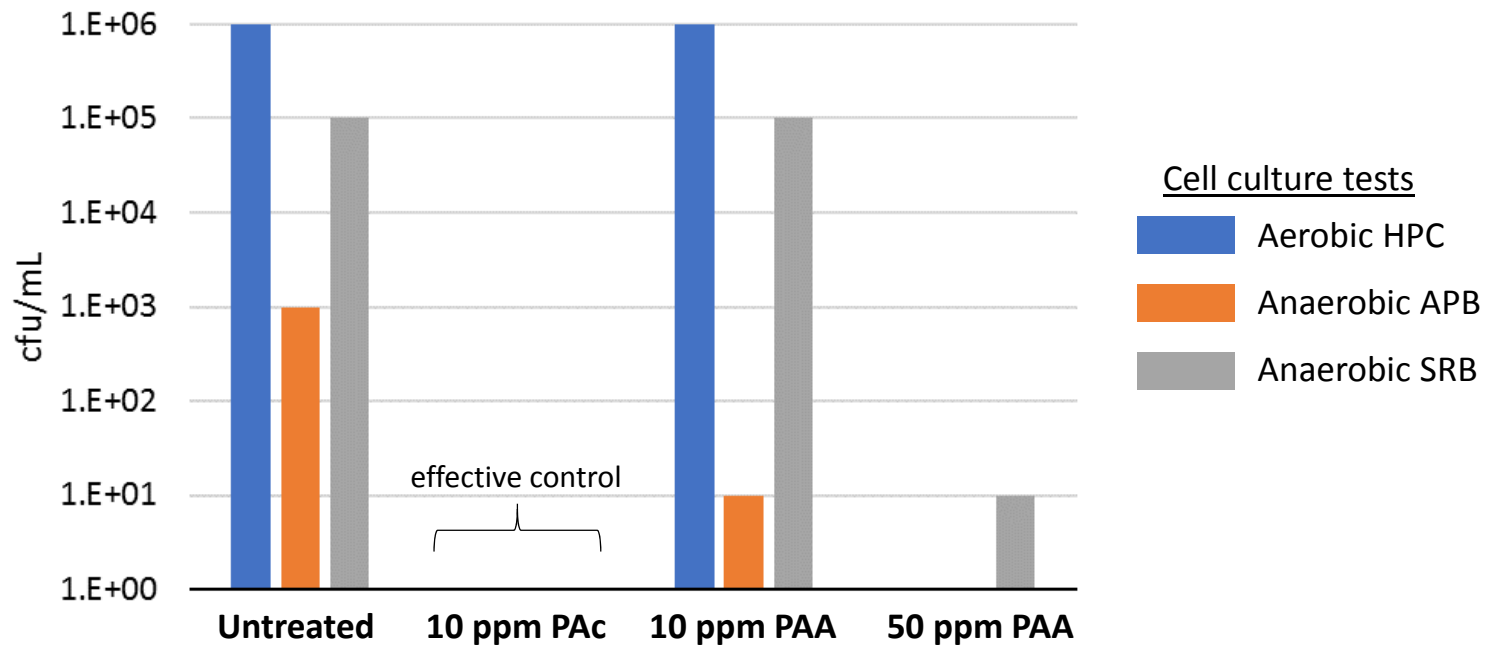
- Similar “active” ingredient structure
- Both industrial oxidants
- Both are effective anti-microbials
- Both are less corrosive than chlorine products
- Both regulated as “alkyl peroxide”
- Both have benign residuals

## How they are different

- PAA is stabilized for storage & shipping
- Peracetate singlet oxygen is transient, cannot be stored
- PAA is highly acidic while peracetate is mildly alkaline and does not have a significant impact on the pH of application
- Peracetate singlet oxygen is effective over a wider pH range
- Peracetate singlet oxygen and PAA differ in their selectivity

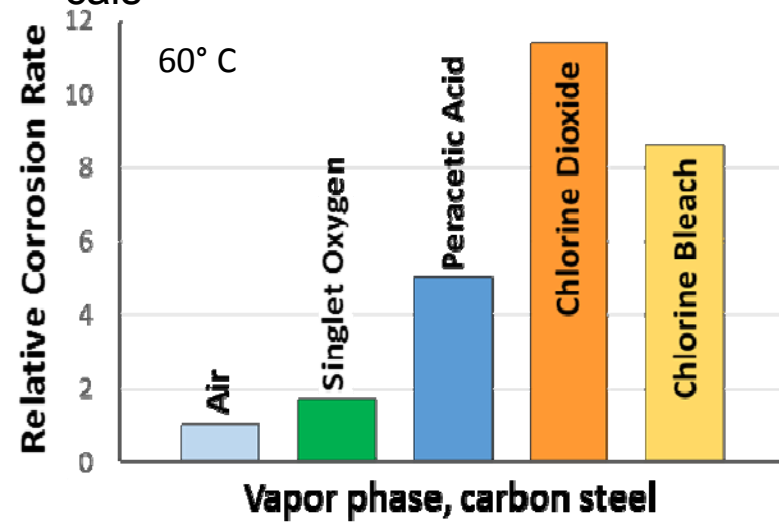
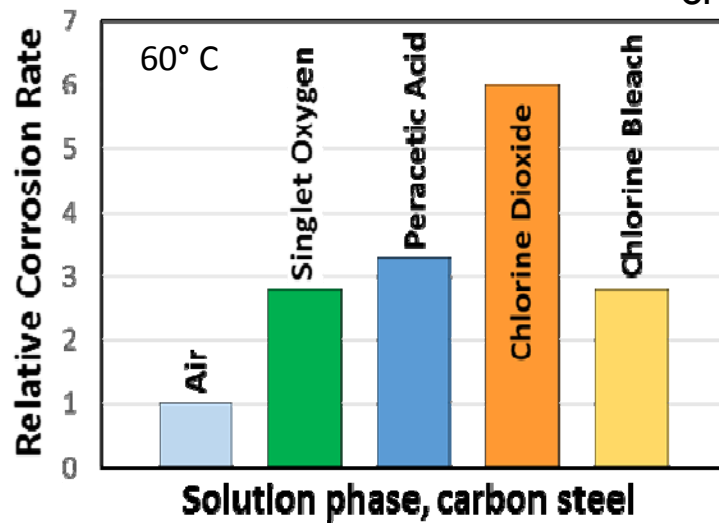
# Microbial Control

Oil-field water containing hydrocarbons, high TDS, suspended solids



# Corrosion

Peracetate is less corrosive than other oxidative chemistries  
Compatible with stainless steel alloys, many plastics, seals and water treatment  
chemicals



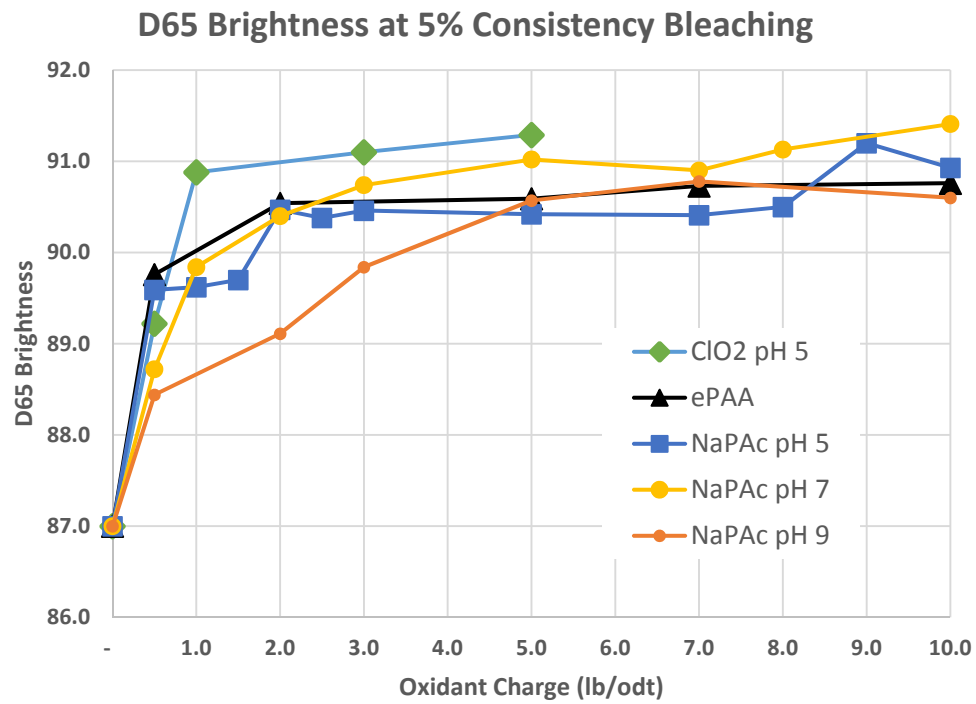
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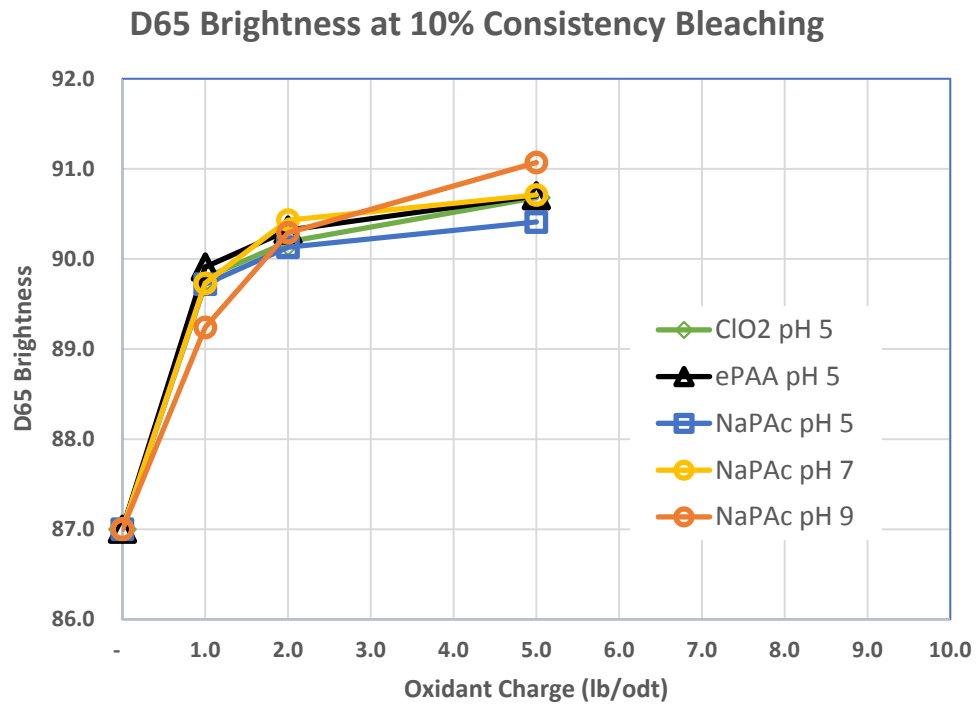
# Laboratory Work Specs

- HW pulp from D-O-D sequence with 87.0% D65 Brightness; sample taken from HD storage tank at pH 6.5-7.0 and 14.2% consistency
- Bleaching Conditions
  - Consistency: 5% and 10%
  - Temperature: 60° C (2 h)
  - Chemical dosage in lbs per ton pulp: 0.5, 1, 2, 3, 5, 7, 10
- Brightening Chemistry
  - ClO<sub>2</sub>: pH 5 terminal pH
  - ePAA: pH 5 terminal pH
  - NaPAC pH 5 terminal pH
  - NaPAC pH 7 terminal pH
  - NaPAC pH 9 terminal pH
- Reversion testing (TAPPI Method T544)
  - Temperature: 90°C
  - Relative humidity: 50%
  - Sampling Times: 4, 8, 24 hours

# Brightening Experiments

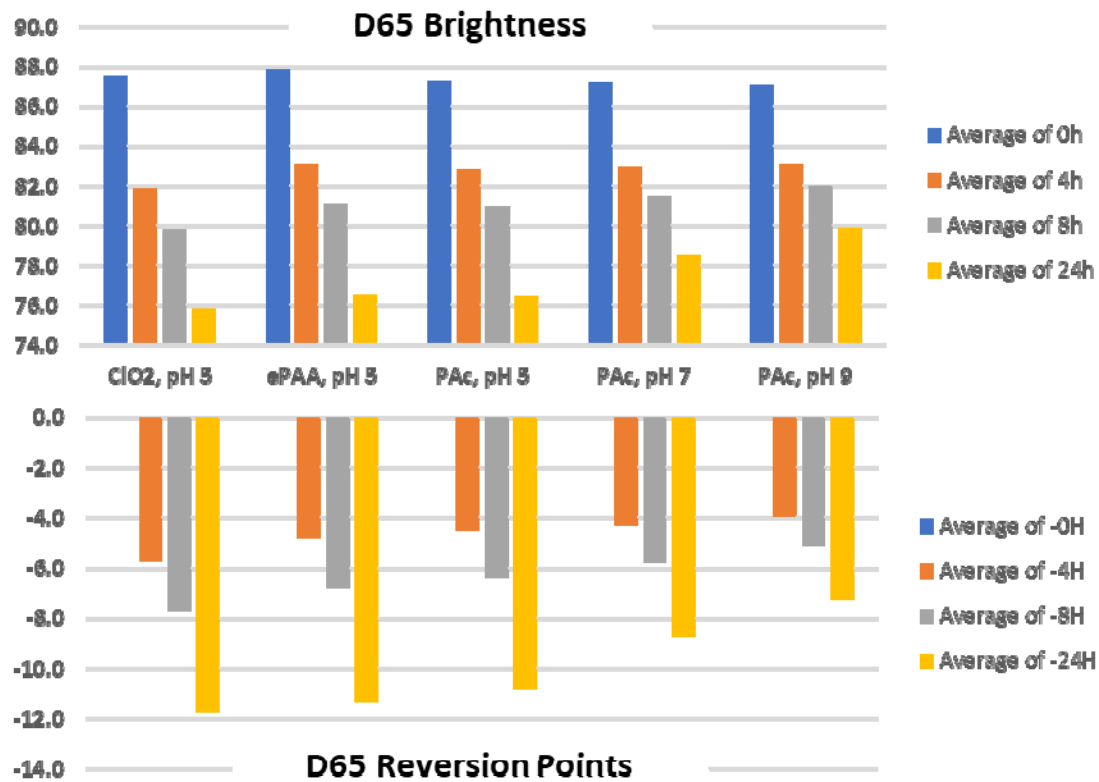


# Brightening Experiments



# Post-Bleaching Brightening and Reversion Testing

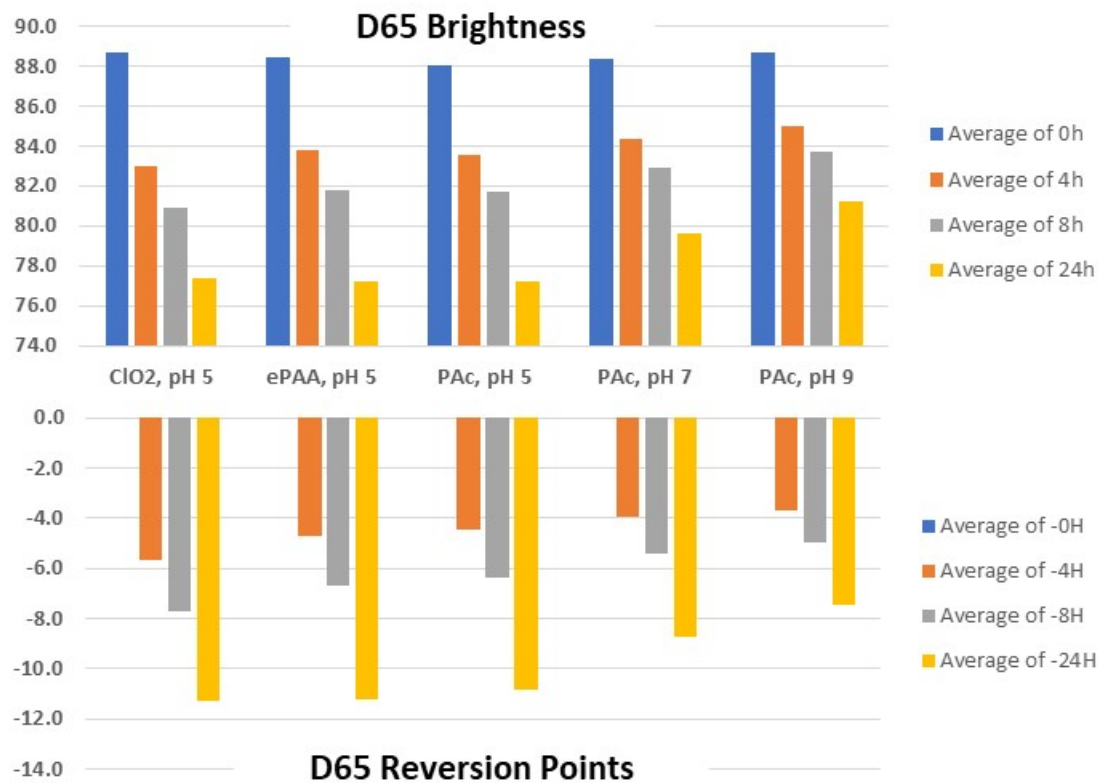
Conditions:  
Oxidant 1 lb per ton





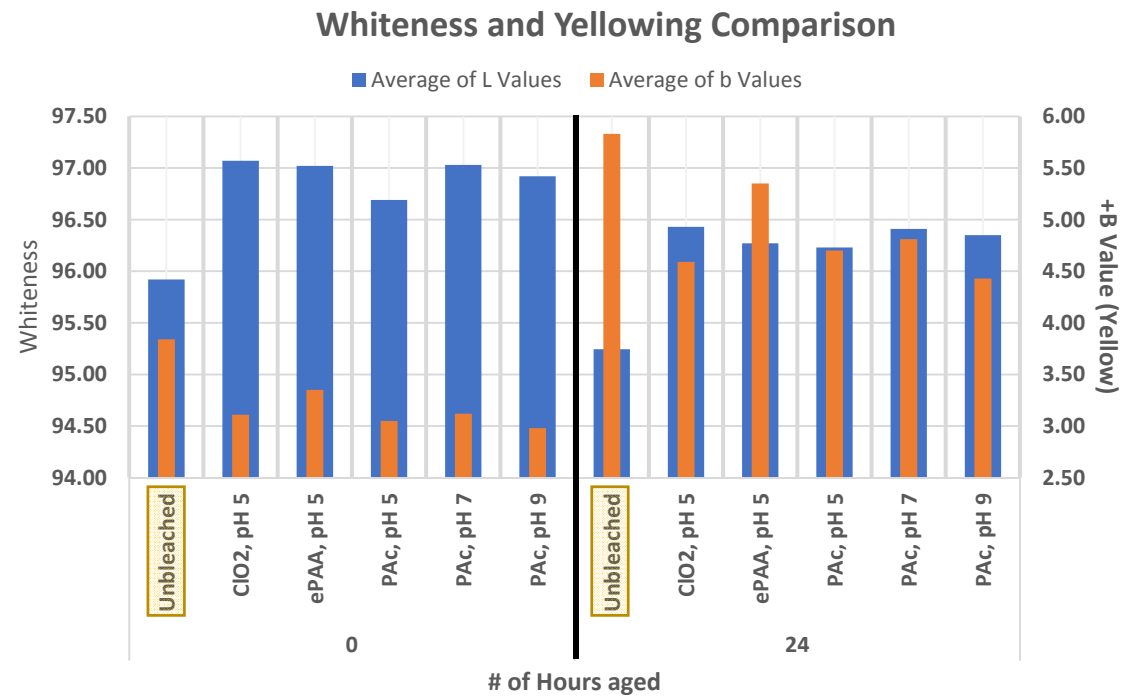
# Post-Bleaching Brightening and Reversion Testing

Conditions:  
Oxidant 5 lbs per ton



# Post-Bleaching Yellowing Comparison

Conditions:  
**Oxidant 5 lbs per ton**



# Presentation Outline

- Clean Chemistry Overview
- Benefits of Peracetic Acid (PAA) for Treating Kraft Pulp
- Peracetate Singlet Oxygen Chemistry versus PAA
- Brightening and Reversion Results
- ➔ • **Conclusions**

# Conclusions

- ✓ Lab studies indicate that peracetate chemistry delivers many of the same benefits realized from peracetic acid
- ✓ Na peracetate singlet oxygen chemistry is now commercially feasible with new onsite production method
- ✓ Na Peracetate chemistry requires little capital investment versus peracetic acid and can be deployed quickly versus other chemistries
- ✓ Na Peracetate chemistry can be safely used in HD tanks at existing conditions making it a drop-in chemistry
- ✓ Na peracetate singlet oxygen chemistry shows promise in a variety of industrial applications as an alternative to traditional oxidants, biocides, bleaching agents
- ✓ Continuing efforts to determine how and where to best utilize singlet oxygen chemistry in pulp & paper processes

Gateway to  
the Future



# Thank You!

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