Novel Biocide Controls Biofilm Formation without Adversely Affecting the Papermaking Process

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ABSTRACT

Strong oxidizing biocides are commonly used to control biofilm formation in alkaline papermaking systems. However, paper streams contain many substances that react with or consume oxidizers (e.g., fiber and starch). Therefore, to achieve effective microbiological control, the oxidizer must be overfed to overcome the effect of these substances. When dosed in this manner, the oxidizer can cause many unwanted reactions and adverse side effects, including the consumption of costly papermaking additives, increased corrosion rates, and reduced felt life. Some oxidizers also contribute to the formation of halogenated organic compounds. When used for biofilm control, strong oxidizers can cause more problems than they remedy.
A patented biocide that effectively controls biofilm without the adverse side effects associated with strong oxidizing biocides is available from Hercules. Spectrum® XD3899 Ammonium Bromide Technology, which can be described as a mild oxidizer, is currently used on more than 300 machines globally and has resulted in numerous production and/or machine efficiency records since its introduction in 2001.

SUMMARY

This paper describes a novel, patented biocide that controls microbial populations without the adverse effects associated with strong oxidizers.

The biocide is "Bromide Activated Chloramine" (BAC) molecule,

which is a much stronger biocide at comparable doses. The low oxidizing potential means that little of the biocide is lost to reactions with the fiber and fillers and thus has high selectivity towards MB populations. The novel biocide provide excellent cost effective control of microbial populations and it quickly degrades into inert compounds before reaching effluent treatment.

The mode of action, application technology, and onsite production process of this Ammonium Bromide - based product are discussed.
Included are case histories to demonstrate the effectiveness of the new biocide. The first case presented is on back end cleanliness of PDF and back water system, shows how the biocide can improve the PM cleanliness and reduce paper breaks. The second case show significant reduction in Sheet spots/holes, thus paper quality improvement.

INTRODUCTION

Papermaking systems provide an ideal medium for bacteria and other forms of microbiological life (MB). To achieve optimum performance of these systems requires that the level of MB contamination be kept below control limits. Failure to control the level of MB can result in large number of problems. The most common of these include:

a) Slime deposits leading to slimes holes and sheet breaks.
b) Catalyze enzyme decomposing residual peroxide in the recycling operations.
c) Anaerobic conditions resulting in excessive odors
d) Generation of Volatile Fatty acids (VFA)

In the past traditional biocides have been used for MB control. However there are several problems when using these "classical" approaches to MB control. The primary areas of concern are:

a) Relatively high cost to achieve the desired level of control.
b) Often, a biocide program will seem to work well for some time and then seems to loss efficiency. This is often mistakenly attributed to the bacteria developing immunity. What is actually happening is the specific mode of action often wipes out the susceptible MB population but this will leave an empty niche that encourages the growth of

different bacteria provided that they are not as sensitive to the biocide.

c) The traditional biocides can be difficult to fully optimize as it's not really practical to measure the level of residual biocide. This is especially difficult in complicated white water loops.

d) Some proprietary biocides exhibit substantive behavior to papermaking furnish and additives, reducing chemical additive efficiency thus resulting higher additive consumption/MT paper. This tends to limit their use to thin stock system.

In the past the alternative is to use oxidizing biocides based on chlorine or bromine, major being hypo-chlorous acid, Hypo-bromous acid. These types of oxidizing biocides are commonly used to control the MB population in papermaking systems with the aim of reducing slime deposit.

These oxidizing agents attack the cell wall directly at a fundamental level, breaking open the cell wall and generally creating havoc in the cell chemistry. For this reason, oxidizing biocides have the advantage of killing nearly all populations of MB at practical concentrations. The principle limitation of oxidizer biocides is the poor selectivity, cause an oxidizer also reacts with the fibers, organics and papermaking additives. To overcome the poor selectivity, the addition rates of traditional oxidizer have to be increased to achieve the free residuals needed to kill Bacteria. This "over addition" causes undesirable reactions with paper making additives, can cause increased corrosion rate.

This paper presents a patented oxidizing biocide that provides reliable, cost effective control of microbial populations without adversely affecting the papermaking process. This paper describes the mode of action, application technology, and onsite production process. Included are two of the many case histories highlighting the benefits of this biocide in different applications of Paper Machine cleanliness and Paper cleanliness improvement.

TECHNOLOGY OF BIOCIDE

Blending a proprietary Ammonium Bromide solution Spectrum® XD 3899, with Sodium Hypochlorite and mill Fresh Water under specific reaction conditions produces the biocide. The biocide must be produced onsite and immediately dosed to the paper system because the biocide begins degrading shortly after production. The production process is completely automated by dedicated reactor cum dosing equipment.

The biocide molecule is "Bromide Activated Chloramine (BAC) ". The process of manufacture allows the bromine atom to remain active to react with bacteria, unlike other haloamines in which the halogen atom is tightly bound and essentially inactive. Like other haloamines the BAC is a relatively small molecule that is able to effectively penetrate biofilm. BAC has low oxidizing potential, similar to a chloramine but is a much stronger biocide at comparable doses and much less persistent with a quicker decomposition rate.

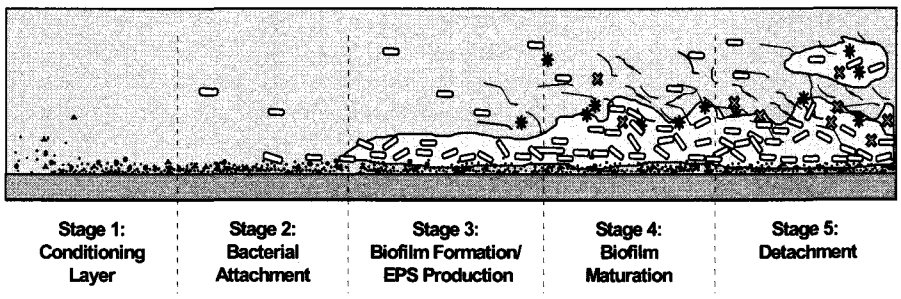
It's important to realize that the low oxidizing potential is actually beneficial as it increases the selectivity of the biocide. If the oxidizing potential was higher, the biocide would participate in a wider range of reactions with fiber/fillers and other organic material, reducing the selectively and the cost effectiveness. The oxidizing potential is still high enough to be a very effective biocide since it acts on the S=S bonds in the cell wall.

These differences translate into a more cost-effective biocide suitable for use in all alkaline or neutral paper making systems.

Mode of Action in keeping paper machine clean

Figure 1 shows the five stages of biofilm formation on a paper machine surface. The BAC works in Stage 2 by killing planktonic microorganisms before they have an opportunity to attach to the paper machine surface. By hindering bacterial attachment in Stage 2, the subsequent formation of biofilm in Stages 3 - 5 are prevented.
This mode of action has been validated in commercial applications.

Figure 1



Excellent biofilm penetration is a feature of this biocide. The biocide is not consumed by the (Exo Poly Saccharides) EPS contained in the slime layer (unlike strong oxidisers that react and are consumed by EPS) and is able to penetrate to kill the bacteria within the slime layer, leading to removal of existing slime deposits.

Application Technology

The biocide can be applied to any alkaline system in a continuous or intermittent fashion. Since the biocide does not react with fiber/additives, it can also be added to thick stock/broke/recycled fiber/ process water systems and even to clean additives before supply tank. Since the volume of BAC dosed per cycle can effect additive concentration, it has to be meticulously planned and doses calculated with limited option of dosing points in additive system, where the additive concentration is not the critical need. The dosage required depends on several factors viz. (fresh water usage, water recycle), MB load and the presence of strong reducing agents. When applied to the paper system in this manner, the BAC provides many benefits. The major features and benefits of this biocide are presented in Table 1.

Onsite Production Process

The dosing equipment blends the Spectrum® XD 3899 "Ammonium Bromide Solution" with Sodium Hypochlorite and Mill Fresh Water in the stoichiometric ratio for reaction, under the required reaction conditions to assure 100%

conversion of the components to BAC. The dosing equipment controls the reaction via PLC to ensure that only the quality BAC molecule is produced (no excess hypochlorite or Amm. Bromide). The major features and benefits of the dosing system are presented in Table 2.

Table 1 – Features and Benefits of BAC Biocide

Features	*Benefits*
• Extremely effective at reducing microbial populations (including filamentous bacteria, unicellular bacteria, yeast and mold, and anaerobic bacteria)	• Reduced sheet breaks • Reduced sheet defects • Increase boilout span • Reduced intermittent machine washup
• Exhibits a low oxidizing potential (weak oxidizer)	• Reduced corrosion rates • Reduced consumption of wet end additives • Does not damage felts • Reduces halogenated organic compounds • Does not bleach
• Is not consumed by organics, ammonia, or other compounds that typically act as demand on oxidizers	• Prevents oxidizer overfeed, which keeps program costs affordable • Oxidizer residuals remain in system for time enough to improve microbiological population control
• Residual is easily measured.	• Simple monitoring can optimize feed rates and prevent excessive program costs
• Degrades readily into non-toxic ions	• No negative effect on activated sludge plants (even at addition rates of up to 10 times higher than normal)

Table 2 – Features and Benefits of Dosing System

Features	*Benefits*
• Programmable logic controller (PLC) ensures formation of BAC, monitors quality parameter, give alarm for any Equipment, Set point, or Control problem.	• Prevents unnecessary waste of biocide - producing chemicals
• System performs automatic shutdown sequence if an interruption of water flow, sodium hypochlorite, or ammonium bromide occurs	• Prevents unnecessary waste of biocide-producing chemicals
• Final product concentration is controlled	• The dilute biocide is not corrosive to skin and does not bleach clothing (Fig.5), which eliminates worker exposure concerns.
• The equipment flushes the feed lines with water after a dosing cycle	• No biocide remains in the lines when they are not in use, which reduces worker exposure concerns

CASE HISTORIES

Commercial applications have verified the effectiveness of this biocide at controlling microbial populations. The following case histories highlight some of the key benefits of this technology, which include reduced wet end deposition, reduced breaks, and TBC reduction by 2-3 Log.

Mill A

An Asian mill producing writing printing Organic biocides were not able to keep the Back water system clean causing deposits in PDF. Reference Figure 2. The BAC biocide replaced the organic biocide treatment and provided the following benefits:

- Extended boilout span – The machine had frequent boilout requirements, since the MB contamination in recovered fiber increased with every passing day after the boilout.
  - Since Spectrum® XD3899 treatment has started, the boilout can be scheduled with planned shuts for preventive maintenance and mechanical / Instrument checks.
- Improved machine runability – The machine runability was poor after about 15 days of boilout. The decision to boilout was based on machine runability. Sometime hose down cleaning was necessary to keep production going.
  - With Spectrum® XD 3899 treatment, the machine runability is consistent and hose down cleaning is not necessary.

Mill B

An Asian Alkaline Fine Paper Machine, had problem of MB dominated deposits in the thin loop system, resulting in Sheet holes. The online hole detector, recording small, medium and large holes showed average 5 Large hole per reel and total 33 PPM of holes, which is now at 1.5 and 6 PPM respectively. Refer to Figure 3.

The Spectrum® XD3899 replaced the competitor's proprietary biocide program at a slightly higher treatment cost, however the benefit of cleaner paper and less finishing house rejection, gave an ROI over 200%. There was substantial drop in the total bacterial counts, refer to Figure 4, from 10e6 to 10e2 CFU/ml. The amount of deposition was reduced dramatically between boilouts. Runability improved and the cleanliness of the paper was much better.

CONCLUSION

The BAC biocide, which is produced onsite by blending Spectrum® XD 3899 (Ammonium Bromide) with Sodium Hypochlorite and mill Fresh Water, offers papermakers an alternative to using Proprietary biocides for microbiological control. This product effectively controls microbial populations without adversely affecting the papermaking process. Proprietary dosing equipment ensures safe and consistent production of quality biocide at the mill site.

Figure 2 - Comparison of machine cleanliness with Spectrum®XD3899.

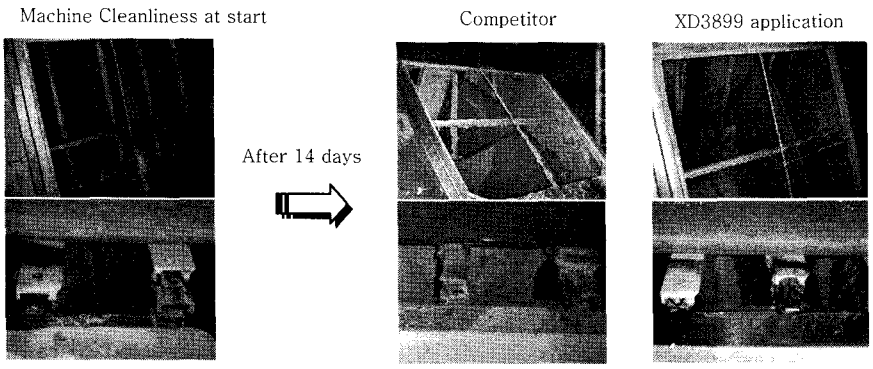


Figure 3 - Reduction in Sheet holes with the use of Spectrum® XD3899.

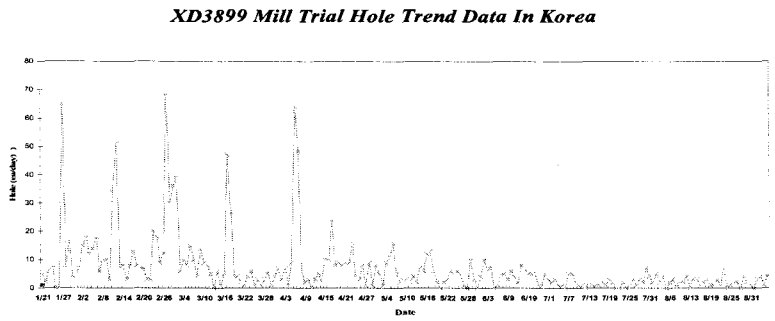


Figure 4 - TBC count in thin Loop with Spectrum®XD3899.

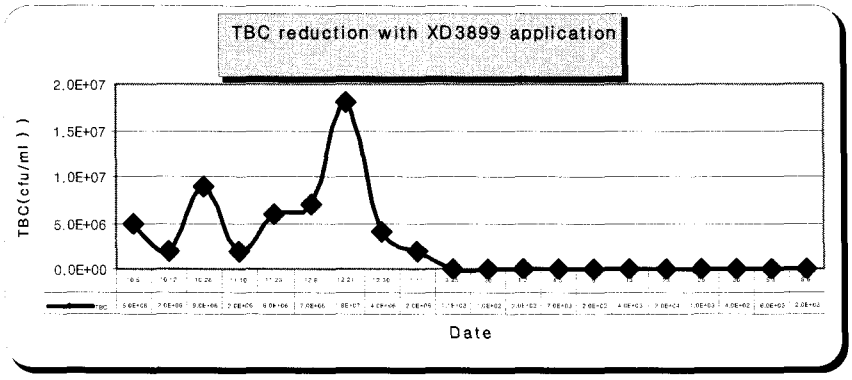


Fig. 5 - Bleaching effect of BAC against HOBr