A brominated methylethylhydantoin slimicide in a tissue mill

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ABSTRACT: The selection of a cost-effective biocide program should be based on efficiency, quality, and safety requirements. Laboratory testing has shown that a novel brominated 5,5-methylethylhydantoin (BrMEH) enhances white water efficacy compared to other oxidizing alternatives. An extensive survey of a mid-Atlantic tissue mill resulted in a number of process recommendations, including an extended BrMEH trial. These trials demonstrated that BrMEH effectively controlled aerobic and sulfate-reducing bacteria while maintaining machine cleanliness and product quality.

Application: Oxidizing biocides may outperform organic biocides in controlling biological growth and product odor.

Marcal Paper Mills is a family-owned business established in 1932. This mid-Atlantic mill produces about 450 tons of napkin, towel, facial, and bath tissue per day. Although the mill purchases some market pulp, most of the pulp used is produced on site in the deink plant. The furnish includes clean office waste, magazines, municipal curbside, and ledger grades. The basic deink plant consists of pulping, screening, washing, oxidative bleaching (using peroxide), and flotation deinking. The pulp is stored in a high-density tank that supplies pulp to a 40-ton/day paper machine and a 200-ton/day paper machine.

As a consumer products company, the mill's primary biocide-related objective is to prevent bacteria from imparting an odor to the finished product. Another objective is to keep its machines clean and running smoothly. If slime builds up on the machines, a disruption of sheet formation can cause paper breaks. Even without breaks, slime can cause quality problems in terms of picking and deposits being carried in the sheet. For these reasons, the mill works to keep the microbiological counts under control.

MILL BIOCIDE HISTORY

At the mill, a number of organic biocides were used to control biological activity during the 1990s, including dodecylguanadine, methylene bis-thiocyanante (MBT), isothiazolone, and 2,2 dibromo-3-nitrilo-propionamide (DBNPA). During this decade, there were periodic episodes of high biological counts and slime problems on the machines. There were also chronic clarification problems in the dissolved air flotation (DAF) units, caused by chemical interference from components of the biocide program.

In an effort to improve results and minimize any potential for product odor, the biocide program was changed to one that was primarily oxidative. Bromine-based oxidizers replaced most of the organic products that were used in the mill, with the result that the biological counts were reduced by a factor of 10. However, there were a number of concerns about the bromine program.

Hypobromous acid was generated on site through the separate feed of bleach and sodium bromide into a common line. These products were fed from tote bins rather than from bulk tanks because floor space was limited in the mill and there were multiple feed stations. Consequently, maintaining the bromine program was labor intensive, requiring an operator to replace tote bins at each feed station on a daily basis. The frequent handling of sodium hypochlorite raised safety concerns for the operators who replaced tote bins and who worked with the feed equipment. Feed problems could also occur, since bleach can produce enough gas to result in air-bound lines. Furthermore, bromine is a corrosive product, and the use of bromine in the mill led to the corrosion of mill pump impellers and stainless steel lines in the system.

BrMEH

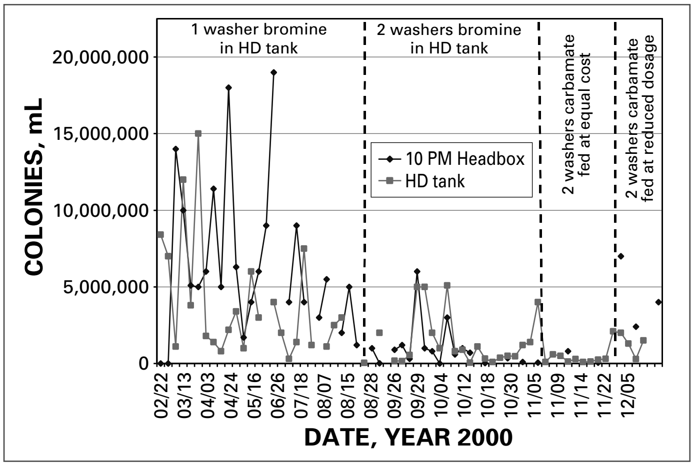
The concentration of biocide has to be high enough and in contact with the bacteria long enough for microbiological control to be effective. A high biocide concentration requires a minimum contact time, while a low concentration of biocide requires longer contact time. Whereas an intermittent-feed program relies on strong concentrations, a continuous-feed program is designed to extend the contact time.

The products of choice for continuous feed-biocide programs are oxidants with chemistries based on direct substitution by halogens such as chlorine and bromine as well as halogen peroxides such as chlorine dioxide. In this case, bromine was selected over chlorine because the high pH of the mill process water prohibited the efficient use of a chlorine-based product.

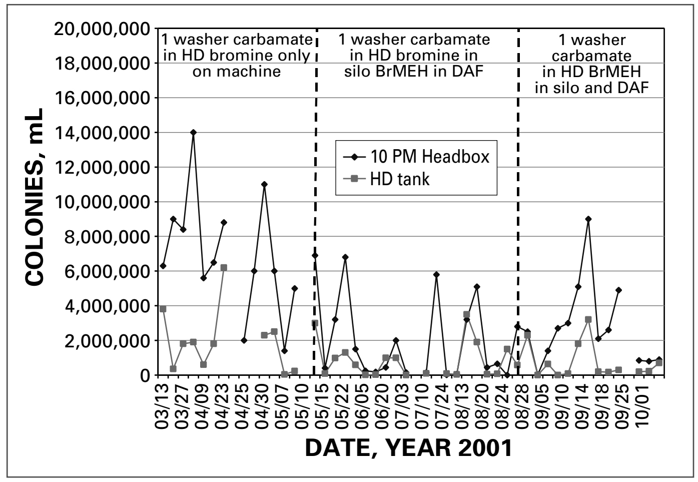
A particular combination of halogenated hydantoins has demonstrated better efficacy than other halogen-based slimicides under both acidic and alkaline mill water conditions [1-3]. This combination includes 1-bromo-3-chlor-5,5-dimethyhydantoin, 1,3-dichloro-5,5-dimethylhydantoin and 1,3-dichloro-5-ethyl-5-methylhydantoin. Here, we will refer to this combination of hydantoins as BrMEH, for bromine methylethylhydantoin.

The improved efficacy of the hydantoins can be explained by the formation of a moderately bound chlorohydantoin species in equilibrium with biocidally active hypochlorite [2]. This equilibrium stabilizes active chlorine in a relatively unreacted combined form, releasing biocidally active hypochlorite on demand. Thus, active halogen lifetime is prolonged, and biocidal efficacy is enhanced. This phenomenon accounts for the superior field results of the product where other inorganic and organic oxidants have failed.

When the binding affinity of halogen is increased, halogen activity and release is further reduced, but biocide efficacy is also reduced because the release of the active hypochlorite is greatly impeded. Thus, hydantoins provide an optimum



1. Biological counts for No. 10 paper machine from February 2000 to December 2000.



2. Biological counts for No. 10 paper machine from March 2001 to October 2001.

balance of reactivity reduction and hypochlorite release, resulting in a very effective water system biocide for the paper industry.

In addition, the potential for total organic halogens (TOX) to find their way into the effluent is reduced because the requirement for applied halogen is reduced. The chance that the finished paper product will be affected is greatly reduced because less oxidant is used and there is less potential for system metals to corrode. The reduction in corrosion potential decreases any potential effect on the Yankee dryer coating and allows the biocide to be used closer to the wet end of the machine.

The environmental fate of any biocide is a major consideration of any slimicide program. A recently published international review of papermaking slimicides gave halohydantoins a favorable environmental profile [4]. This conclusion was based on the rapid detoxification of active halogen species and the low toxicity of the unhalogenated residuals. BrMEH is rapidly converted to residual nonhalogenated hydantoin and a halide ion salt. Testing has also indicated that BrMEH hydrolyzes completely in water. Other halohydantoins follow similar pathways, and their degradation products are of a similar low toxicity.

BrMEH is a granular product that can be produced with a high active content. It is easier to handle than liquid oxidative biocides and does not require as much labor.

SURVEY OF THE MILL

A complete survey of the mill was performed, and process flow diagrams were developed. Recorded parameters such as retention times, system temperatures, pH, chest volumes, and flows were considered in the treatment strategy recommendations. An historical background of biological counts was developed through the use of plate counts of various samples drawn from 34 different mill locations. Samples were also submitted to an off-site laboratory that performed toxicant evaluations and odor testing.

The toxicant evaluation work identified BrMEH as possibly superior to the bromine toxicant used on the machine. However, it also became apparent that the overall performance of biocides in the mill could be improved by making some mechanical changes and replacing some products. These changes were made first.

A review of the survey data identified the high-density storage tank as a critical location in the mill for the biocide program. The plate counts for the paper machine were directly influenced by the conditions in the high-density tank. The success of the machine program was dependent, then, on success in controlling microbiological growth prior to the high-density tank. The high-density storage tank has a retention time of approximately 12 h. This additional time in the high-density storage tank makes it appropriate for slower-acting biocides to be considered part of the overall biocide treatment program.

Samples taken from the stock line to the high-density tank were analyzed (**Fig. 1**), and there was evidence of carryover of Formamidine Sulfinic Acid (FAS) by-products from the bleach plant. These reductive by-products contributed to an environment that promoted the growth of anaerobic and facultative anaerobic microorganisms. It was also determined that bromine being fed in the line was being rapidly consumed by the FAS by-products, leaving the high-density tank unprotected against biological contamination.

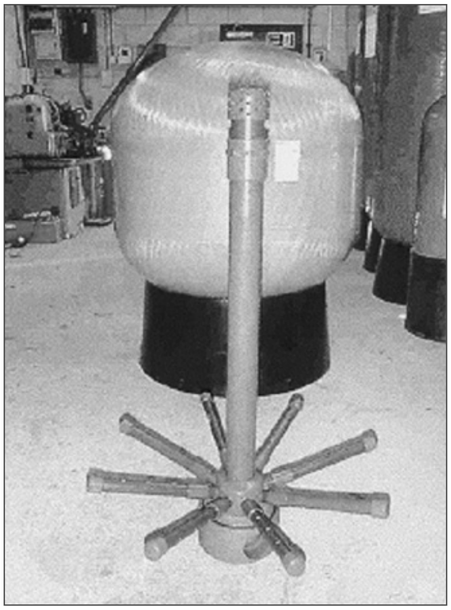
Based on these observations, a recommendation was made to move the FAS feed point from the second steam mixer to the first. This change made it possible to use two washers instead of one for removing FAS by-products. Finally, the bromine application for the high-density tank was replaced with a reductive biocide, carbamate, to eliminate the consumption of biocide by these by-products.

IMPROVEMENTS PRIOR TO BrMEH

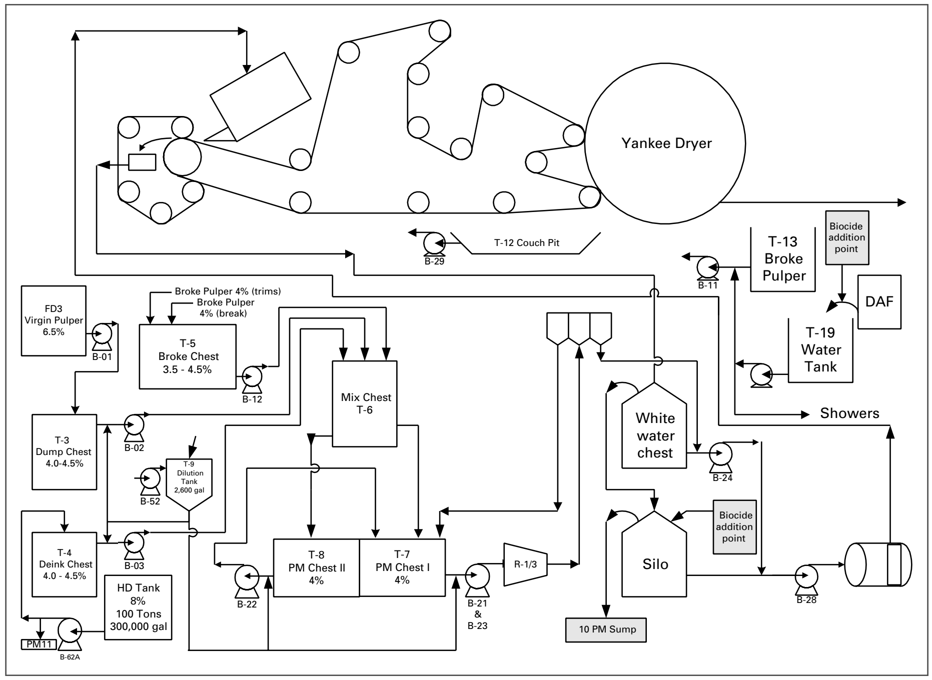
The mechanical improvement in the bleach plant provided for an 85% reduction of FAS by-products in the high-density tank. As Fig. 1 shows, this change led to bacteria counts that were lower and less erratic. When carbamate replaced bromine as the biocide for the high-density tank, biological control improved further.

This improvement allowed for chemical savings in the mill. The carbamate dosage was reduced by 40%, bromine dosages on the machine were reduced by as much as 25%, and the organic biocide application (isothiazolone) was successfully eliminated from the machine biocide program.

The feed of FAS to the first steam mixer led to a drop in brightness, since the No. 1 tank was too small to provide enough retention time to complete the FAS reaction. The FAS



3. From the bottom of this feeder, water flows up through a bed of granular BrMEH. The water flow and temperature are controlled to dissolve biocide to the proper concentration.



4. Diagram of the No. 10 paper machine, showing addition points for the biocide.

feed point had to be relocated back to the second steam mixer, which resulted in higher bacterial counts (**Fig. 2**). The improved chemical program did allow for the reduced biocide dosages to be maintained, however.

The mill personnel plan to consider options that would allow for the use of the larger tank for the FAS reaction, while two washers are used for removing byproducts. The cost of the pipe reconfiguration in the bleach plant will be weighed against the financial advantage of the improvement. By this time, however, sufficient data had been collected to proceed with the BrMEH trial.

BrMEH feed system

BrMEH is a solid product that is fed through an enclosed feeder (**Fig. 3**). Water flows from the bottom of the feeder, up through a bed of product in the feeder, and on to the application point. The dissolution of product can be accurately maintained at proper levels through the control of water flow and water temperature.

An automatic temperature controller, using a thermostat that is interlocked to a steam valve, controls the water temperature. Steam is injected directly into the water stream on demand, maintaining temperatures within 2F° of the set point on the controller.

The water flow is maintained on the discharge side of the feeder with a PVC ball valve and is measured with an in-line meter. The feed rate of product can be accurately calculated using the flow rate and the total halogen residual in the feeder effluent. This residual can be easily measured with a simple test kit that utilizes powder reagent pillows and a color wheel.

BrMEH trials

To further reduce program costs, improve results, and eliminate the concerns related to the use of bromine, mill personnel began trials with BrMEH. Trials were initiated in the belt press shower water line and in the effluent stream from the DAF unit of the No. 10 paper machine (**Fig. 4**). The product was fed at dosages representing a 10% savings over the cost of the bromine applications.

The first two applications were chosen to minimize the impact on production of any unforeseen problems that might have occurred during the trial. During the course of the trial, samples were periodically collected from various sample points, and standard plate counts were performed for heterotrophic bacteria. The data served as a means of tracking the performance of BrMEH and to compare its performance to that of bromine when HOBr was being administered.

The data showed a reduction of average biological counts in the shower water and from the No. 10 paper machine. At this point, a decision was made to replace the last remaining bromine application on the No. 10 paper machine—the machine silo—with BrMEH. Once again, the product was fed at a dosage that represented a 10% savings in cost over the previous bromine program. After this change was made, the machine bacterial counts dropped again relative to the counts for the high-density tank. This improvement is shown in Fig. 2.

Halogen residuals were measured in the silo before and during the trials. Both products were applied at levels below halogen demand, however, so no residual was observed with either program.

CURRENT PROGRAM AND FUTURE PLANS

The benefits realized with the use of BrMEH include:

- A 10% reduction in biocide cost
- Improved safety (because a strong oxidizer is no longer in the feed lines)
- Reliability (elimination of pump failures)
- More consistent feed of product
- Less labor required
- Reduced corrosion potential
- Reduced biological counts.

The changes improved the mill's biocide cost considerably. The biocide cost to the mill in 1999, when bromine was being used as the primary biocide, was more than 50% higher than the cost of the program that is now in place.

The mill plans to continue to replace bromine with BrMEH on other machines and throughout the mill. Dosages and feed points will be optimized to meet mill objectives. A reductive organic biocide will continue to be used for the high-density tank, and efforts will be made to return to a two-washer system for the removal of FAS by-products in the bleach plant.

CONCLUSIONS

The use of oxidative products in a biocide program was superior to the use of conventional organic biocides for the control of odor and microbiological growth. However, the application of oxidizers in conjunction with a reductive bleaching process has to be carefully controlled.

For an oxidizing program to be effective, the mechanical removal of reductive bleaching by-products needs to be optimized. If used appropriately, a reductive organic biocide can complement the oxidizing program. Bromine will successfully control biological growth in a mill, but there are problems related to the application of bromine.

BrMEH was used to successfully replace bromine. The use of BrMEH improved the control of odor and microbiological growth at a reduced cost. The feed of BrMEH was more reliable, and the use of BrMEH made it safer for mill employees. The labor required to maintain the BrMEH product was much less, and the new product reduced the potential for corrosion. **TJ**

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INSIGHTS FROM THE AUTHORS

As water consumption decreases in paper mills, it becomes more and more important to have a microbiological control program that contributes to the overall success of the mill. We chose to consider this novel chemical approach as a promising way to improve the biocide program at a tissue mill. Our main concerns were preventing odor in the paper product, preventing slime buildup, and improving employee safety.

This work follows from the previously published work of Phil Sweeny and Michael Ludensky. They reported on the laboratory evaluations, and their results have now been applied in a tissue mill.

The most challenging part of the work was developing a reliable feed system. With the system, mill personnel had to be able to monitor and control the dosage easily for the biocide to do its work at the proper concentrations.

We were surprised by the tremendous improvement in control gained when the mill implemented the recommended changes in the process. The laboratory work indicated the residual FAS bleach was adversely affecting the biocide program. One recommendation was to change the FAS feed point, but the improvement was more dramatic than we expected. Mills that are currently using a bromine-based microbiological control program may be able to gain many of the same benefits that were gained at Marcal.

Our next step is to expand the application of the BrMEH technology around the mill by replacing conventional bromine and bleach applications to maximize the benefit for the mill.

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