ISSN: 0379-5462
IPPTA: Quarterly Journal of Indian Pulp and Paper Technical Association
Vol. 31, E1, 2019, pp.8-11

Controlling Microbiological Growth and Foul Odors in Pulp & Paper Industry

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ABSTRACT

Papermaking systems provide a moist, warm environ¬ment that is rich in nutrients for microbiological growth. The high nutrient and contamination levels associated with the incoming recycled fiberand reduction in water reuse leads to increased microbiological growth. The recycled fibers often contains residual sizing, coating, starches, polymers, and adhesives, which are rich in nutrients. This recycled fiber is also contaminated with higher loading of microorganisms, which is not the case with the virgin pulp. The biofilm generated by aerobic bacteria can form massive slime deposits that can be an inch or even more in thickness. When these deposits break loose and fall into the paper furnish, they result in end product imperfections such as slime holes and defects or even in slime breaks. The rapid growth of aerobic organisms willalso deplete the oxygen content of the stock and water system producing, hydrogen sulfide, methane and/or volatile fatty acids.A reduction in fresh water usage and recycling of the process water also accelerates microorganisms' growth and related problems including generation of odorous chemicals, microbiological influenced corrosion and faster slime buildups on paper machines. When the system becomes more anaerobic, most biocide programs fail to perform well. This is mainly due to the inability of these biocides to deal with a very high level of contamination in a reductive environment. This paper reveals the changes in micro-organisms population in wetend section as a result of furnish change and higher water closure and the mechanisms and problems caused bysuch changes. The emphasis is also made to understand and deal with the problems related to the generation of foul odors. This paper also discusses possible solutionsand our experience to deal with such problems.

Microbial Slime Outbreaks

In papermaking process, the wet-end section is considered as nutrient rich environment. Together with warm temperature and longer retention time, this creates an ideal environment to support microbiological growth. Many additives in papermaking can be consumed by bacteria and fungi and allow rapid expansion of the population. The fast growth of microorganisms overload the wet-end with mass of microbial biofilm that causes serious problems to machine runnability and sheet quality such as slime breaks, slime holes, downgraded papers, as well as higher wash-ups and unscheduled shuts.

Part of the microbial slime problem is an overgrowth of filamentous bacteria. This is a collective name for group of bacteria, which have filament-like shapes. Their body is made of array of cells grouped together in a long filament structure and protected by a thick layer that protect them from extreme environmental conditions. This protective layer makes filamentous bacteria, as shown in Picture 1 and 2, less sensitive to biocide attacks hence difficult to kill. Many of these filamentous bacteria are also active biofilm producers. The overgrowth of filamentous bacteria creates tangled web of filamentous mass covered with sticky layers of biofilm. They easily traps/captures other papermaking materials in wet-end area and ends up as a massive deposit all over the paper machine surfaces. Some of this filamentous bacteria develop yellowish-pinkish-orange pigment and the slime produced commonly known as pink slime.

Picture 1. *Stringers caused by Filamentous bacteria*

Picture 2. *Slime spots in finished paper/board. Changes to purple color with slime test reagent.*

Overgrowth of Anaerobic Bacteria

The micro-organisms are frequently grouped according to their ability or inability to grow in an environment containing oxygen. The aerobic organisms readily grow in such an environment while anaerobic organisms de¬velop most favorably in an atmosphere in which the dissolved oxygen approaches zero. In an Oxygen rich environment such as in highly agitated stock and white water, aerobic bacteria flourishes.

Slime outbreak in paper machine is strongly related to overgrowth of aerobic bacteria.

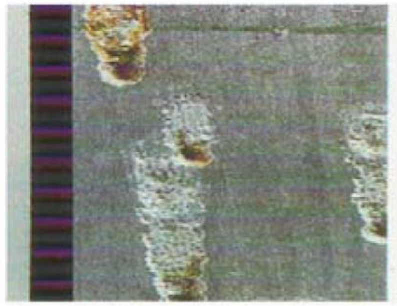
The overgrowth of aerobic bacteria can also deplete the oxygen content of the stock and water system, especially in locations where agitation or penetration of oxygen from air is low. As the oxygen disappear, the condition is becoming more favorable for growth of anaerobic bacteria. As the trend continues for mills to close their water circuits, water temperature often increases while dissolved oxygen content in water decreases. The lower concentration of dissolved oxygen creates a more favorable growth condition for anaerobic bacteria. Various problems are related to the overgrowth of anaerobic bacteria including Microbiological Induced Corrosion (Picture 3 and 4), spoilage of additives and stock, foul odors in process due to the presence of volatile fatty acids and hydrogen sulfide, and production of explosive/flammable methane gas in pulp/furnish chests. All these problems are caused by the metabolic end products generated by anaerobic bacteria. In some cases, the odor problem also happens in finished paper and paperboard affecting finished product quality.

Many of the anaerobic Clostridia species produce cellulase enzymes. The cellulases degrade the cellulose polymers found as structural components of plant materials such as wood. If furnish is exposed to these cellulases, especially for extended periods of time, the structural integrity of the wood fibers may be sacrificed due to enzymatic activity. Loss of this structural integrity can lead to a decrease in sheet strength. Anaerobic colonization of broke towers has also been implicated with decreases in sheet brightness.

In addition to the factors mentioned above, the use of sulfite bleaching of recycled de-inked fibers neutralizes the function of most biocide chemistries.

Picture 3. *Slime inside shower bar rich of iron sulfide deposit–an indication of anaerobic growth*

These biocides are affected by the presence of reducing agents and cannot function properly when the residual levels of sulfite bleaching agent increases in the recycled deinked pulp. Therefore, a different biocide program strategy is required when dealing with de-inked pulp furnish.



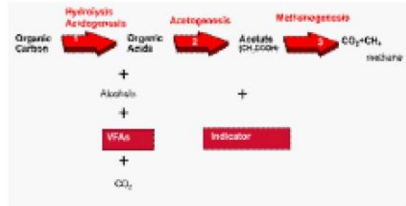
Picture 4. *Pitting corrosion caused by microbiological attack*

Mechanisms of Microbiological related Odors Anaerobic degradation of organic materials leads to the intermediate formation of Hydrogen sulfide and volatile fatty acids (VFA) - primarily butyrate, valerate, propionate and acetate (Picture 5). The volatile fatty acids release pungent and unpleasant odors both in the process and in the finish products. The VFA related odors have been reported in various grades of paper / board / tissue causing serious financial losses as the final products are being rejected by customers or end users.

The chemical makeup and physical properties of many of paper additives form an environment conducive for microbial growth. Microbial spoilage can change the properties of the additives or cause physical or chemical changes that are detrimental to their use in paper making.The starch degradation negatively affects strength and causes loss of brightness after the size press or in coatings (due to reducing sugars the starch turns brownish) besides strong sour odor. The proteins degradation in a coating is malodorous and color changes due to microbial byproducts.

The water system closure has a profound influence on odor problems. The various chemicals are likely to be recycledwith the process water while few years ago, they were flushed out hence did not cause any problems. On the plus side, the costly additives and fines are retained more, energy is conserved and water treatment costs are reduced. However on the negative side, there is an increased problems with odors.

As a result of microbiological activity in the secondary treatment, the clarified water from waste water treatment plant



Picture 5. *VFA as an intermediate in anaerobic degradation process*

continues to get rich in residual bacteria, VFA, and various bacterial extracellular enzymes. In fact, VFA is present in big amount as it is the intermediate compound for complete degradation of organic chemistry in the anaerobic process into methane. When the methanogenesis reaction is not present or not running completely in waste water treatment plants (WWTP), the VFA cannot be converted into methane and will finally get accumulated in WWTP. This will cause strong VFA odor in WWTP area and the water discharged from WWTP will also carry strong smell. Often it will cause complaints for foul odor from the communityliving near mill's area. When the clarified water from WWTP is reused in the wet-end process, the VFA will increase the potential of odor problem in the wet-end process as well as in finished products.

Controlling Microbiological related Odors From microbiological point of view, there are several effective methods to prevent or control the buildup of microbiological contamination in the paper machine and WWTP areas, which include improvement in mechanical treatment, paper machine housekeeping and operation, WWTP operation, and through chemical actions (biocides or odor neutralizer)

Mechanical Treatment Preventing the odor problem requires implementation of root cause analysis to identify what led to the odors in the first place. If the odor has a microbiological basis, the logical first step is to reduce the environmental factors favoring the growth of the microbes. The effective way to reduce odor caused by microbial activity will be to avoid VFAs and H2S being formed under anaerobic conditions. Without proper VFA mapping, it may be difficult to trace the origin of the VFAs and H2S in the process. The available technology should also be used for monitoring by-products of the anaerobic activity.

To minimize VFA and H2S production and related problems in the system, an adequate oxygen concentration in the system should be ensured. Good water circulation, direct aeration, and avoiding stagnant water are all actions that can be easily implemented. The VFA and H2S mix well in the process flows. When stock and white water circulate throughout the process or agitated properly, this will increase air penetration into water hence minimizes the growth of anaerobic bacterial. Therefore it is important to ensure sufficient agitation inside the chest to maintain good oxygen concentration in water. The arrays of white water chests with cascade (gravitational) alignment also help to increase oxygen concentration in water. The oversized chests/tanks are not ideal as this will establish dead flow areas hence boost the anaerobic growth in that particular chest.

Although the chest ventilation will not stop the generation of volatile gases by anaerobic bacteria, it will minimize the buildup of these gases and limit their concentrations to below the explosive threshold. Many chests are vented or have a manhole that can be opened whenever the chest stagnates. Ideally the chests should be permanently vented and periodically checked to assure that the vent is not plugged. This is especially important during shutdown. Ventilation in area of high oxidant vapors is recommended as this will help to avoid unnecessary accumulation of these vapors and reduce vapor phase corrosion potentials in these areas.

Paper Machine Housekeeping and Operation Implementing an effective machine cleaning or boilout is very crucial for the success of any microbiological control program. Since the old biofilm deposit also provides seed for the next production batch, it is important that such deposits must be removed before the next production cycle to maintain desired machine runnability and finished product quality. Further we can expect that the accumulation of deposits will be faster when mill closed its water circuit. It should be noted that inhibition/removal of biofilm deposits will also contribute to generation of anaerobic activities as it creates a barrier for oxygen penetration while diffusing inwards. This effect has been demonstrated in relatively thin films less than 0.2 mm thick. On many occasions, the mills only conduct shortloop boilout while the long loop boilout conducted once or twice a year. The cleaning/boilout program must be carefully designed to address the most troublesome deposits, executed effectively using a selected chemical treatment, and monitored closely to ensure maximum impact.

During mill shutdowns, aerobic bacteria quickly consumes the dissolved oxygen present in the white water hence provide low oxygen environment, which is ideal for the growth of anaerobic bacteria. Agitating the water in the chest or by aerating the water with an air-line can help to maintain the oxygen level at a desired level. If the water is allowed to stagnate, oxygen will be consumed quickly and anaerobic bacteria will thrive. However, this is not a recommended practice for stock chest as aeration will encourage the growth of aerobic bacteria during longer shutdown (more than eight hours) leading to high aerobic bacteria count during machine startup. The stock preservation biocide is recommended to avoid high micro-organisms growth during long machine shut.

Maintaining an optimum chest/tower operating level can also help to control microbiological growth. Keeping high level of stock means higher retention time available for bacteria to grow and multiply, which will change this stock to become a bioreactor. Big stock towers have potentially poor mixing hence create stock channeling problem. The stock in the center flows faster than the stock on the sides of the tower wall hence encourage fiber spoilage and slime accumulation. Once the stock level drops, the spoiled stock and slime accumulated on the side of the wall will also collapse, which in turn will contaminate the stock for papermaking.

Waste Water Treatment Plant Operations The control of foul odors in WWTP area can be achieved by optimizing the function of each process stage followed by a continuous review of each operating and control parameters to make required corrections wherever needed. The design parameters must be used for comparison purposes. If the problem persists, then changes of process design should also be considered. The prevention or a reduction in malodor formation may be achieved by preventing the anaerobic growth in the aerobic stages, minimizing retention in systems where there is no aeration, such as in holding tanks or rising-main sewers. The aerobic conditions can be maintained in some cases by the addition of air, oxygen, or oxidizing agent.

In order to reduce the formation of sulfide in the treatment and handling of sludges, a reduction in the input of sulfate or modifications to the treatment processes is highly recommended.The addition of biocides has been used to reduce the high contamination of Sulfate Reducing Bacteria (SRB) growth of sewer wall slimes. Moreoversulfide neutralizers are used to degrade and/or convert H2S into non smelly sulfur compounds.Use of oxidizers can also be considered to oxidize H2Sand volatile organic sulfides inthe sewage or sludge when conditions become aerobic. This will help to prevent high load of smelly H2S in aeration tanks and secondary clarifiers. The hydrogen sulfide may also be controlled by an addition of precipitants, such as iron or zinc salts.

Biocide Treatment The management of microbiological activity is very important in allowing the papermakers to succeed in controlling microbiological related odors and its impact on the finished products. The biocide treatment needs to change from a traditionally "deposit focused" approach to an overall aspect of microbiological related problems including the ones from anaerobic bacteria. Type of biocide actives used in the program may need to be changed as well and the monitoring program should include parameters such as anaerobic growth. One of the major drawbacks in the use of most biocides is their inability to perform satisfactorily when dealing with a very high load of contamination and the reducing environment commonly found in the production of recycled paper and board. Some biocidesthat worked well in the papermaking process with virgin pulps and in open systemsmay no longer be products of choice for recycled pulps or mills with higher water closure. Therefore toxicant test for biocide selection should be conducted again to determine if the best products are being used for the current environment. In addition, due to the high competition in recycled paper markets, some recycled grades can only afford the use of relatively low cost chemical programs. Proper product selection tests should be conducted to identify the most cost effective microbiological control program required to meet these different challenges.

During a mill shutdown, aerobic bacteria quickly depletes the oxygen level in the white water and converts it to an anaerobic environment. If stock is held formore than eight hours, aerobic populations will increase, providing a large inoculum to the paper system on startup. The stock chests often require a stock-preservation biocide to control aerobic populations during a mill outage.

Odor Neutralizers

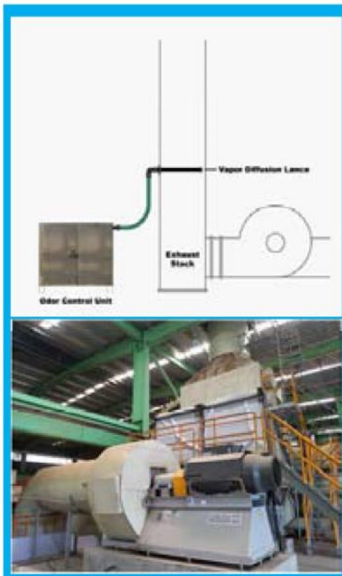
There are many other non-biocide chemical applications that can be used for microbiological related odors. They can be divided into two main groups: vapor-phase technologies, used for the control odorous compounds in the air or gas; and liquid-phase technologies, used in controlling odorous compounds in the liquid at the source itself.

The vapor-phase technologies, as shown in Picture 6 and 7, typically are used in point-source applications to prevent the "leakage" of odorous air from stacks, vents, manways, access hatches or other areas. The discharge from the ventilation system is the only route for the odorous air to escape. Therefore it must be treated. The vapor-phase systems are very effective at preventing fugitive emissions from the ventilated sources and preventing odor problems associated with those sources. The chemical is mixed with water, pumped through pipes/hoses and delivered via nozzles or fans to areas affected by the odor. After the solution droplets are dispersed into the air, they neutralize odors on contact. The major advantage of atomization nozzle systems is the level of control they provide. Through various means of control, depending on system style and design, the volume of product dispersed can be regulated.

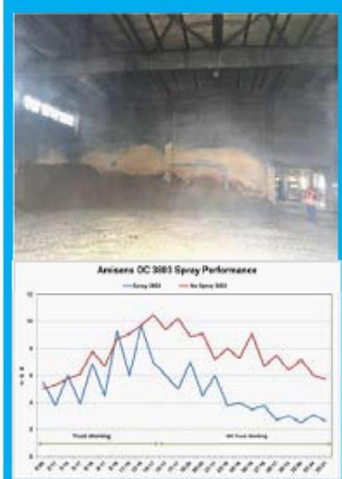
The liquid-phase technologies typically are used in water collection, storage, sewer, scrubber and condensate cooling systems with high concentration of soluble, odorous agents. A wide range of chemicals can be chosen to selectively react and neutralize the targeted organic odors. Since the chemicals are added closed to the source, this treatment is highly effective as it reacts directly and specifically with the odorous agents. The neutralization of odorous chemicals in recycled water or condensate allows safe and convenient reuse of these waters for various purposes. In a scrubber system, wet-gas scrubbing can remove or change the chemical composition of odorous contaminants while contacting the gas in a liquid-phase process. The contaminants either react with or dissolves in the liquid before getting removed in the liquid-phase. A careful selection of scrubber liquors is needed to ensure effective odor removal and ease of operations. The sulfide neutralizer product can also be used to recover the brightness of dark furnish due to sulfide generation by SRB in addition to removal of rotten egg smell.

Case study on the use of Sulfide neutralizer product

A mill experienced the blackening of stock coming out from the stock towers. Moreoverthe stock also had a foul smell. The presence of black contaminants lowered the brightness of finished paper. The black furnish and foul smell is the result of growth of sulfate reducing bacteria (SRB). The mill agreed to trial AmiSense product addition into the stock storage tower at various dosages to look for the most cost effective treatmentwhile continuously monitoring for brightness,ORP and sulfate/sulfide levels. After 30 minutes of contact time, a positive change in brightness was observed. For details, refer to the Picture 8.The trial result shows that the stock brightness improved significantly. At 300- 500 ppm dosage of AmiSense product, no rotten egg smell was also detected in the paper.



Picture 6. Example of odor neutralization via spray on dryer section vapor going to stack / chimney.



Picture 7. Odor neutralization via spray in effluent dry sludge collection room in a paper mill. The odorous gas concentration reduced by 50-60% after the application

Program Monitoring

For monitoring activities of anaerobic bacteria, test of sulfate reducing bacteria and VFAs are often used in the field. With increased water reuse, the demand for anti-microbial oxidants and certain proprietary biocides may also increase. In many cases, it may be beneficial to use biocide active which works in reductive environment. A combination with oxidizing biocide can be applied to boost the system ORP and destroy the odor causing chemistries. Process or product odors, additive-preservation problems, pH swings, and corrosion could be routinely profiled as these data can signal the presence of large populations of anaerobic or facultative bacteria in the process. The use of portable gas testers and other test kit to measure concentration of odorous agents both in water phase and air phase should be considered as part of an improved control strategy.

Picture 8. The handset test shows that the brightness of the dark furnish (marked as "0") gradually increases after addition of AmiSense product.

Summary

In pulp and paper industry, the odor related problem needs significant attention from papermakers as it causes severe financial losses due to the finished product/s being rejected by the customers. The odor may originate through many different sources. Some of the odor problems are microbiologically induced, which become more severe with an increased use of recycled fibers and closed water systems. But with careful choice of raw materials, improved mechanical operations and housekeeping followed by an effective application and monitoring of biocide and odor control chemicals, it is possible to maintain lower odor levels in the papermaking process and final products.The chemical applications should be care¬fully designed to achieve maximum effectiveness and economics from such programs.