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Eliminating Foul Odour in Recycled Paper Production

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Abstract:

Odour in kraft paper is a matter of concern for both manufacturers and consumers alike. Increasing e-commerce sales (on-line shopping) has resulted in increased use of paper packaging which sometimes produce a bad odour especially when delivered in air-conditioned rooms. Even after delivery the packages continue to emanate a foul odour, which is obnoxious for the environment.

It is also noted that often the paper coming off the machine has minimum or no odour but the foul odour develops on storage or after shipment. This causes a problem for 'converters' as well as 'exporters'. Foul odour from packaging papers is also unacceptable for packing food items or luxury items like perfumes.

The Papermaking system provides a moist, warm environment that is rich in nutrients, highly suitable for microbiological growth.

Added to this is increased contamination associated with the incoming recycled fibre.

Recycled fibres contain residual sizing agents, coating agents, starches, polymers, and adhesives – components that all provide a congenial platform for bacterial growth.

However it is the reduction in fresh water usage and water recycling which is the main contributing factor for the 'odour' problem.

Rapid growth of aerobic organisms depletes the oxygen content of the stock and water system. This low oxygen content creates a reductive environment which favours the growth of anaerobic bacteria. Anaerobic bacteria can produce hydrogen, hydrogen sulfide, methane, and volatile fatty acids. All of these contribute to the generation of odorous substances in addition to microbiologically induced corrosion, and faster slime buildups on paper machines.

It is also observed that most biocide programs fail to perform well when the system tends to become anaerobic. 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 discusses the changes in type of micro-organisms population in the wet end resulting out of furnish change and higher water closure. Emphasis is on measures to control generation of foul odours.

Keywords: *Anaerobic Bacteria , Volatile Fatty Acids (VFA) , Sulfate Reducing Bacteria (SRB) , Biocides , Odour Scavengers.*

Introduction

The Papermaking wet end is considered a nutrient rich environment for bacteria. Together with warm temperature and long retention times, it creates an ideal environment to support microbiological growth. Many additives used in papermaking also support growth of bacteria and fungi and thereon allows a further rapid expansion of the population. Slime breaks, slime holes and papers with foul odour are all a result of microbiological activity.

'Foul odour' development also occurs when the paper comes in contact with atmospheric moisture especially in a confined space.

This can happen when the paper is being shipped for export or stored over a long period of time.

Environmental regulations have pushed the paper industry towards Zero Liquid Discharge (ZLD) systems.

The demand for higher strength in Paper have pushed the consumption of substantial quantity of starch which is primarily being used at the Size Press.

Starch is one of the best nutrients for microbial growth. Moreover, since the starch film remains on the paper surface as long as its life, it tends to absorb atmospheric moisture over time, leading to development of a foul odour due to generation of microbes.

Mechanism of Odour Formation

i) Source of Odour

Foul odour in kraft paper is attributed to the following reasons.

- Increasing closure of the Paper machine circuit in order to conserve water and aim towards "Zero Liquid Discharge".
- Increasing use of starch both in the wet-end as well Size Press in order to increase 'strength' of Paper.
- Increased use of Chemical additives.

The above factors lead to an increase in microbial activity, especially anaerobic bacteria – the main source of 'Odour'.

Anaerobic conditions produce the following types of Odour.

Volatile Fatty Acids (VFAs)

- Acetic Acid – Odour of vinegar.
- Propionic Acid – Odour of stale cheese
- Butyric Acid – Odour of Rancid Butter.
- Formic Acid – Odour of Formaldehyde

VFAs are fatty acid with less than 6 carbon atoms. They are produced by both facultative and anaerobic bacteria. Clostridium genus is the main VFA producing bacteria found in paper. It is an Obligate Anaerobe meaning that oxygen is toxic to them. It is also endospore forming. Mature spores persist even after the bacteria is dead.

Sulfate Reducing Bacteria (SRB)

- Odour of Rotten Eggs (smell of H_2S)

The Foul Odour in Paper is a combination of VFAs and SRBs. It is very difficult to distinguish between the two odours.

Moreover, there is a continuous Redox reaction taking place between the two. SRBs use VFAs as electron donors to get reduced and further reduce Sulfates.

Sulfates when reduced produce H_2S gas. VFAs get oxidized. (Propionic and Butyric acids get oxidized to acetates).

Hence the type of Odour is constantly changing

Note: Low VFAs may not correspond to Low Odour

ii) Measuring Odour

The Nose is the only equipment available for measuring Odour. It is very subjective in assessment. Measurement of VFA is also subject to the reaction taking place with the SRB.

Low VFAs may not correspond to low Odour. It is better to check the microbial contamination instead of VFA alone.

Assessment of type of bacterial load is possible in a Lab or on-site.

Bio-control Programme

i) Aeration

Odour development in the papermaking water circuit is due to VFAs and SRBs. Both are due to activity of Anaerobic bacteria. The only way to control Odour is to check the development of such bacteria. Anaerobic bacteria develop in the absence of air. Good aeration is therefore necessary to prevent growth. Water in chests and silos should not be allowed to remain stagnant when there is a machine shut. They should be kept under constant agitation.

ii) Keeping system Clean

In order to control growth of micro-organisms and prevent odour development it is necessary to eliminate the deposits in the system which may be acting as nutrients. Hence, periodic Boil-out of the system is necessary. If complete Boil -out is not possible, at least a short loop cleaning should be performed periodically. It is recommended that an Oxidising Cleaner should be used along with a hot alkaline solution. This will ensure removal of all biofilm deposits which become a repository for moulds and fungus. It is also necessary to clean the starch preparation tanks as well as Size Press tanks in the same way.

iii) Use of Biocides

Biocides are products that kill microorganisms or inhibit the growth of microorganisms which are responsible for 'Foul Odour'.A good Biocontrol Program can increase machine efficiency, extend boil out times, reduce papers breaks and sheet defects and also control 'Odour' as compared to non-use or use of a poor biocidal treatment.

iv) Types of Biocides

Broadly classified as

- Oxidizing Biocides
- Non-oxidizing Biocide
- Odour Scavengers

Oxidizing Biocides

Oxidising biocides act by destroying the cell wall of the microbe. Common oxidisers are Sodium hypochlorite (NaOCl), Bromine compounds, Chlorine Dioxide., Peracetic acid, Ozone etc.

1. Chlorine Dioxide

Among all oxidisers , Chlorine dioxide has gained importance since it is found to be the safest and most effective chemical for control of microbiological growths in paper mills water circuits. Unlike Chlorine it does not give rise to polluting products like Trihalomethanes (THMs) .It is particularly effective in systems having a high pH, ammonia-nitrogen contamination, persistent slime problems, or where the microbial contamination is aggravated by contamination with vegetable or mineral oils, phenols or other high chlorine-demand producing compounds.

Chlorine dioxide, is a chlorine-based chemistry which is safe for both domestic and process water treatment. Its ability to be successful in all types of makeup water make it an attractive choice. It can penetrate both sessile and planktonic levels of the biofilm.

It is less aggressive than chlorine but a potential drawback is that a generator may be required to produce the chemical on site.

Physical properties of Chlorine Dioxide: -

- Molecular weight of 67.45.
- Gas at normal temperatures and pressures. Readily soluble in water.
- Melting point of −59 °C.
- Boiling point of 11 °C.
- Yellowish/green and has an odour similar to that of chlorine.
- Denser than air and is water soluble at standard temperatures and pressures up to 2500 ppm.
- Explosive in air at concentrations greater than10%.

Benefits of Chlorine Dioxide:-

* Chlorine dioxide is a very effective slime control agent.
* It can destroy bio-films.
* In the gas phase it can decompose explosively. For this reason, it is generated at Point of use.
* By controlled mixing of the two components Sodium Chlorite and HCl, along with water, it is possible to optimize feeding dose of ClO_2 to 2 to 3 g/L.
* Chlorine dioxide reacts rapidly and can be applied at a site immediately before the problem area, unlike many conventional antimicrobials, which are generally slow acting.
* Chlorine Dioxide remains relatively unreactive with the vast majority of organics, reducing the dose rate necessary to achieve effective control.
* Low dose rates result in typically low corrosion rates when compared to other oxidizers. In addition, minimizing or eliminating the slime layer reduces microbiologically influenced corrosion on equipment.
* The chlorite ion (chlorine dioxide by product) keeps working as both a bacteriostat and slime control agent, even after the chlorine dioxide has reacted.
* By effectively controlling slime growth, the frequency of boilouts can be reduced and the potential for unscheduled downtime because of paper breaks can be minimized.
* Effectively controlling slime growth minimizes the hole count, maintaining the quality of the finished sheet.
* Odours resulting from bacterial fermentation, phenols, sulfides, or mercaptans are virtually eliminated by use of chlorine dioxide.

Since chlorine dioxide is used for potable water disinfection, it is appropriate to use this versatile disinfectant in food grade paper applications. Food grade paper is required to meet higher microbial standards than fine paper. Therefore, the cost of microbiological control is considerably higher than for fine paper. This is because it is difficult to inactivate bacterial spores, particularly the genus Bacillus, which survive the extreme temperatures of the dryers in the papermaking process. Chlorine dioxide has been found to be a very effective sporicide in food grade paper applications, in potable water applications, and in some food processing applications Unlike chlorine, chlorine dioxide is relatively non-reactive with most of the organics found in alkaline whitewater. As a result, a large portion of the chlorine dioxide fed will be available for disinfection. Thus, the bacterial activity can be effectively reduced to almost any desired level by controlling the chlorine dioxide feed rate. ClO_2 is a reactive oxidizing gas.

2. Bromine Based Oxidising Biocides

* Bromine is an oxidising Biocide
* It attacks micro-organisms by destroying their cell walls.
* It is less corrosive than Chlorine.
* Does not produce harmful substances like Chlora-amines.
* Unlike Chlorine it is also active at higher pH.
* Has a broader kill spectrum.
* Bromine based biocides are highly effective in preventing and removing bio-film.
* They are also effective anti-viral agents.
* They are also effective against algae, fungi, and moulds.
* Bromine compounds are activated by compounds such as NaOCl (Hypo) to release HOBr which further dissociates to release active Bromine (OBr-).
* It is necessary that enough Sodium Hypochlorite (NaOCl) is present to release the Bromine. The ratio: NH4Br : NaOCl (10%) = 1:4
* Chlorine oxidises the Bromine compound releasing active Bromine which is a powerful Biocide.
* $NH_4Br+NaOCl=NH_4Cl+NaOBr$
* $NaOBr + H_2O = HOBr / OBr- + NaOH$

Biocide + Hypo should be added together preferably through a static mixer.

3. Non-Oxidizing Biocides :

* These Biocides are more varied in nature.
* The active ingredient can vary from product to product.
* They can be broad spectrum or specific.
* Effective by slug dosing in wet-end.
* Used in Size Press to protect starch film.
* Since microbes can build-up immunity, Biocides with different actives can be rotated for obtaining best results.
* Some examples of Non-oxidising Biocides : Isothiazolinone ; Glutaraldehyde; DBNPA ; Bronopol ; Quats etc.

Conventional methods of Odour control include use of Oxidising and Non-oxidizing biocides (antimicrobials). An effective treatment program for slime and Odour control may involve both oxidizing and non-oxidizing biocides. Since the biggest culprit for imparting 'Malodour' in Kraft paper manufacturing is starch, which Chlorine Dioxide alone may not be able to tackle, hence use of specific Non-oxidising Biocide becomes mandatory.

4. Odour Scavengers

Not considered as Biocides , nevertheless they help control Odour. They are Montmorillonite clays such as Zeolites which can adsorb odour. The natural mineral is purified, micro fined and chemically treated to enhance Odour adsorption properties.

Salient Features: -

* Highly active.
* Three-dimensional open structure.
* Average particle size: < 7 micron.
* Can effectively remove a broad range of odour / VOC molecules.
* Effective against sulphurous odours.
* These products are freely water dispersible and can be used in the wet-end.

In order to control 'Odour' Paper Industry needs to take a holistic approach by focusing on

i) Cleanliness of system : Regular boil outs /Cleaning of paper machine system, starch tank, size kitchen etc.

ii) Use of Oxidising and Non oxidizing Biocides. Since Microbes have a tendency to develop immunity with particular biocides, selection of proper biocides and using in rotation by shock dosing is necessary.

iii) Odour Scavengers : use of speciality organo-clays.

BIO-CONTROL TESTING PARAMETERS

Bio-count: Using Bactaslydes

BS-101 can be used for TBC and Yeast + Fungi'

BS-115 is used for testing SRB.

ORP (Redox potential)

Minimum or Negative ORP indicates presence of high amount of Anaerobic bacteria.

ORP should be around 180mV in approach flow.

Dissolved Oxygen (DO)

Low DO enhances activity of Anaerobic bacteria.

DO should be around 80%.

VFA (Volatile Fatty Acids) :

Should be as low as possible.

Conductivity

Presence of Bacteria raises conductivity. A good Bio-control program should bring down conductivity

Conclusions:

Paper mills need to take a holistic approach towards Odour Control by improving housekeeping, timely and effective boil outs, managing proper water circuits for reuse of water, use of Coagulants and Flocculants to minimize the suspended solids and impurities. It has been observed that modified and activated montmorillonite clays such as **Zeolites** and **Bentonites** have a capacity to adsorb colloidal impurities. Users of such products report less odour problems. The odour may originate from many different sources. Most odour problems are microbiologically related, and becoming more severe with the higher use of recycled fibers and water reuse. However, by careful choice of raw materials, improved housekeeping followed by effective application and monitoring of biocide programme ,it is possible to keep paper processes and products odour free. The chemical applications should be carefully investigated to achieve maximum effectiveness and contribution to the performance and economics of the programme.

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