ELIMINATING FOUL ODOUR IN RECYCLED PAPERMAKING

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Introduction

Today, most paper manufacturers have moved towards producing paper in a closed loop system in order to conform to Zero Liquid Discharge (ZLD) and conserve water and energy. At the same time huge quantities of starch is being used at the surface to improve the 'strength' of paper.

These measures have led to 'new' challenges.

Prime among them has been the Problem of 'Odour' in Paper.

The 'closed' papermaking system along with added starch provides an environment rich in nutrients, highly conducive for microbiological growth.

Efficient odor control is achieved through 1) Sanitation, 2) Aeration ,3) Use of Biocides in Wet-end and Size Press 3)

Factors leading to ‘Odour ’ formation.

1. **Starch** : Addition of large quantities of starch in Size Press contributes majorly to the generation of bad odour in paper. Nowadays, testliner and fluting paper mills use starch (40 – 60 Kg per ton of Paper) to increase strength and BF in the final Paper.

2. **Closed water loop** : ZLD processes lead to a build up of contaminants coming from the waste paper. These provide necessary nutrients for growth of Anaerobic bacteria., leading to the production of Volatile Fatty Acids (VFAs) and Sulfate Reducing Bacteria (SRBs) which are responsible for unpleasant odours.

3. Anaerobic Conditions : Low oxygen conditions also favour

Odour Problem in Paper

- Foul Odour is a combination of VFAs & SRBs. There is a constant Redox reaction between the two. VFAs get oxidized by SRBs. SRBs reduce Sulfates to produce H2S.
- Hence type of odour is always changing.

- **Testing for odour :**
  There is no all- inclusive chemical tests or equipment to measure odour.
  Olfactory (smell) tests are the only conclusive test for odour.

- Measure of VFA and SRB indicates presence of odour forming compounds, but does not pinpoint the exact source.

- ORP in the positive side indicates a healthier system.

Bio Control Program

1. Periodic boil outs and Cleaning of Starch tanks and Size press
2. Ensure aeration and avoid stagnancy in water circuit.
3. Using Chlorine Dioxide for rapid action against microbial growth
4. Using Non-oxidising Biocides in Starch solution in Size press application
5. Using Bactaslydes to check presence of SRB , TBC , and Fungal spores.
6. Monitoring effectivity using measurement tools : ORP ; VFA, Residual Oxygen etc.

Bio Control Parameters

1

Use of Bactaslydes

- BS 101 for TBC and Yeast + Fungi
- BS 115 for SRB

2

Redox Potention (ORP)

- Minimum or –ve ORP indicates anerobic bacteria.
- ORP should be positive : around 100 mV in approach flow

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Volatile Fatty Acids (VFA)

- VFA should be as low as possible.
- Under 250 is considered ok for ZLD plants

Chlorine Dioxide

An Oxidising Biocide

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Chlorine Dioxide

- Mode of Action

- Chlorine dioxide is a yellowish-green gas with a high oxidation capacity.
- Unlike other oxidizing agents, ClO_2 is selective in its reactions, allowing it to target specific microorganisms without causing significant damage to the substrate.
- W.H.O considers Chlorine Dioxide as the most potent and the safest water sanitizer. It is also **FDA approved** and can be used in Food Contact Paper.
- Unlike Sodium Hypo Chlorite and Chlorine, it does not give rise to polluting products like Trihalomethanes (THMs)
- Its mechanism involves the disruption of microbial cell walls and interference with cellular functions, leading to rapid inactivation.

Chlorine Dioxide - Mode of Action

- ClO_2 decomposes explosively in air at concentrations above 10%.
- Hence it is prepared on-site by controlled mixing of individual components and HCl along with water. Concentration of ClO_2 generated is 1 to 3 g/L
- The introduction of ClO_2 in paper mills involves multiple stages, targeting both microbial growth and odor control.

1. Pulp Preparation

- Introduction of ClO_2 prevents the proliferation of bacteria that produce malodorous compounds such as hydrogen sulfide and mercaptans.
- By reducing microbial populations, ClO_2 ensures that the pulp remains relatively odor-free.

Chlorine Dioxide - Mode of Action

2. Wet-End

- The wet-end of the paper mill is particularly prone to microbial contamination due to the high moisture content.
- The use of ClO_2 as a biocide helps maintain a balanced microbial ecosystem, minimizing the formation of biofilms and the production of VFAs.
- ClO_2 also reacts with sulfur compounds, neutralizing odors without compromising the chemical properties of the paper pulp.

3. Water Treatment System

- Paper mills today recycle and reuse water, making effective water treatment essential for preventing odor emissions. ClO_2 is utilized in the water treatment systems to control microbial growth.

Chlorine Dioxide - Advantages

- 1. **Superior Efficiency** in killing bacterial and fungus without damaging the fibers.
- 2. ClO_2 can be integrated into existing production systems with minimal modifications. It is effective at low concentrations, reducing the need for large amounts of chemicals and thus **minimizing operational costs**. Its solubility in water also makes it easy to apply various stages of the paper production process.
- 3. As compared to traditional chlorine-based biocides and others, ClO_2 has a **lower environmental footprint**. It breaks down into harmless byproducts making it a more sustainable option for odor control in paper mills. Its low dosage requirements further reduce the risk of harmful residues accumulating in the final product or being released into the environment.

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Biocides for Size Press

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Biocide

Mode of Action

- Today, Starch serves as a cost-effective and biodegradable adhesive that enhances paper strength, printability, and smoothness.
- However, starch-rich environments are susceptible to microbial contamination, as starch provides an ample nutrient source for bacteria, fungi, and mold.
- These microbial populations can produce volatile compounds during metabolic processes, leading to the development of odors that affect the quality of the paper. To combat microbial contamination and resultant odors, we have developed specialized biocides to be used along with starch in the size press applications.
- These specially curated biocides disrupt cell membranes without the high reactivity associated with oxidizing agents. These biocides are often preferred for starch applications due to their stability and prolonged activity in aqueous environments.

Biocide

Mode of Action

- Chlorine Dioxide has effectively replaced harmful biocides such as Sodium Hypo Chlorite due to its better efficiency and ecological footprint.
- W.H.O considers Chlorine Dioxide as the most potent and the safest water sanitizer. It is also **FDA approved** and can be used in Food Contact Paper.
- Starch applied on Size Press also needed a biocidal treatment to prevent generation of odour forming compounds..
- Some paper manufacturers found complaints of odour in paper even after using Chlorine Dioxide in the wet-end.

Measures to Control Odour in Paper

- A Paper Mill in Hyderabad was already using Chlorine Dioxide but was still struggling with an Odour problem. They asked us for a solution.
- We carried out an extensive microbiological study of the Paper as well the Starch being used to determine the source as well as the type of bacteria and fungi which were present. We found that the Starch itself was responsible. After coating it provided a nutrient rich environment for further growth of bacteria and fungus .
- Recognizing the problem, we curated a biocide that acts best to mitigate the type of bacteria and fungus which were prevalent. It also had a prolonged action which protected against microbial growth even through storage and transportation.

RESULTS:

Test Description	Macroscopic observation	Growth Promotion Test			Identification of Predominant Microorganisms
		Presence/ Intensity of Bacteria	Presence/ Intensity of fungus	Presence/ Intensity of Sulphite reducing bacteria	
Paper Sample 1	No Visible discolouration	Not detected (++)	Detected (+++)	Detected (+++)	**Bacteria:** *Bacillus spp.* **Fungus:** *Rhizopus spp.* *Mucor spp.* *Penicillium spp.* *Paecilomyces spp.*
Paper Sample 2	No Visible discolouration	Not detected (++)	Detected (++)	Detected (++)	**Bacteria:** *Bacillus spp.* **Fungus:** *Rhizopus spp.* *Mucor spp.* *Penicillium spp.*

- : No growth
\+ : Trace growth
++ : Moderate growth
+++ : Heavy growth

Case Study 1

Case study 1

Test Liner Paper Mill - Capacity - 300 TPD

Furnish – 100% recycled fiber

Location - Hyderabad

	Blank	Day 2	Day 10	Day 30
Chlorine Dioxide in Wet End	2 ppm	2 ppm	2 ppm	2 ppm
Biocide in Starch	0 g/ Mt	150 g/ Mt	150 g/ Mt	150g / Mt
Biocide in Wet End	0	0	0	0
VFA	980 mg/ ltr	785 mg/ ltr	595 mg/ Ltr	465 mg/ ltr

Prior to trials, we conducted a hot alkaline wash of the Starch tanks and Size Press with our Oxidising Cleaner. (pH =9.5 Temp : 70C. Oxidising Cleaner : 1Kg per M3)

Results of Case Study 1

- As you can see, The Paper Mill was already using Chlorine Dioxide still VFA was 980 mg/ ltr.
- After using Biocide in starch for 2 days, VFA dropped by almost 25% .
- After 10 days, VFA was reduced by 40%.
- After a month of using biocide in Size press, VFA came down to almost half of the original reading, from 980 to 465 mg/ltr.
- Currently, we plan to start dosing another oxidizing biocide in the wet end to further reduce the VFA to below 300 mg/ltr.

Case Study 2

Case study 2

Test Liner Paper Mill | Capacity - 310 TPD

Furnish – 100% recycled fiber

Location – North India

	Blank	Day 2	Day 10	Day 30	Day 60
Chlorine Dioxide in Wet End	0 ppm	3 ppm	3 ppm	3 ppm	2 ppm
Biocide in Starch	0 g/ Mt	150 g/ Mt	150 g/ Mt	150g / Mt	150g/ Mt
Biocide in Wet End	0	150g/ Mt	150g/ Mt	150g/ Mt	100g/ Mt
ORP (mV)	- 452	- 398	-285	-15	+ 110
VFA (mg/ltr)	1475	1245	1095	825	342
Bacteria Count	10^7	-	10^5	10^3	10^2

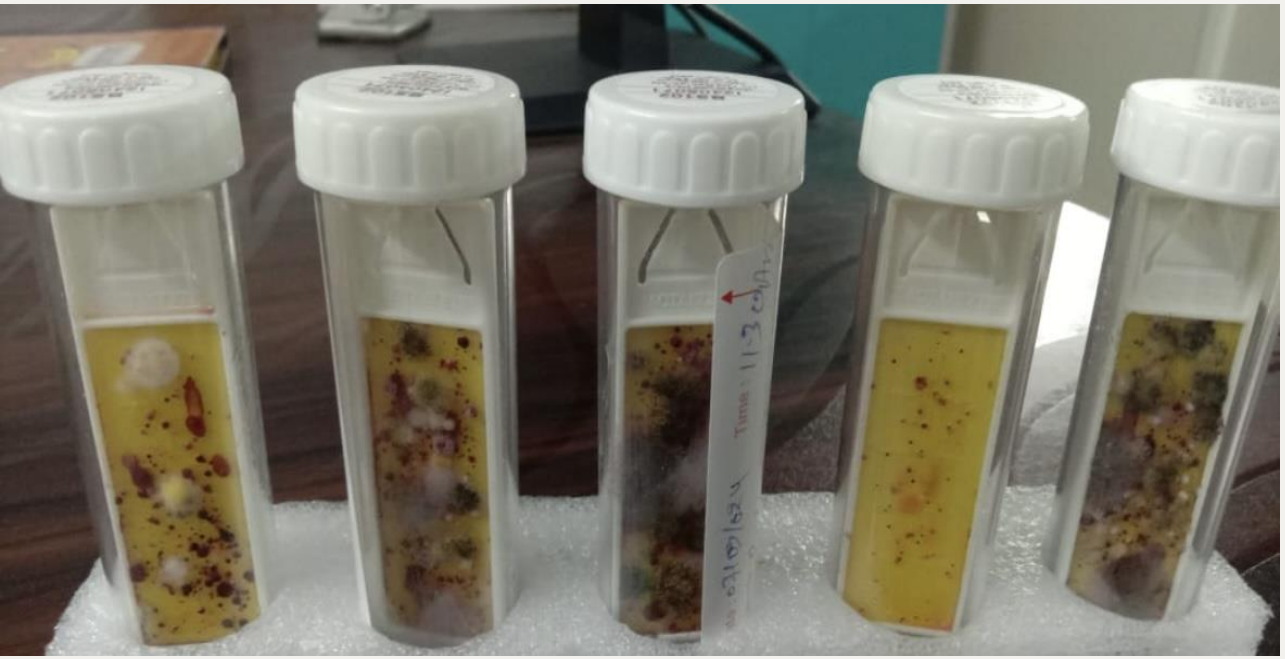
Prior to trials we conducted a hot alkaline wash of the Starch tanks and Size Press with our Oxidising Cleaner. (pH =9.5 Temp : 70C. Oxidising Cleaner : 1Kg per M3)

Case study 2

Test Liner Paper Mill | Capacity - 310 TPD

Furnish – 100% recycled fiber

Location – North India



Results of Case Study 2

- In this Case, the Paper Mill was not using any Biocide or Chlorine Dioxide. Hence, the VFA was as high as 1475 mg/ltr since it was ZLD
- ORP was negative 452. Bacteria Count in the Head Box, Silo, as well as ETP water was 10^7 which showed a very high level of contamination.
- After incorporating Bio Control Program, in the first week itself we observed that VFA was reducing slowly, and ORP was rising.
- Since in this case the paper mill was not using any kind of bio control program, the contamination was very high and it took more than a months time to bring the ORP levels to the positive side. The VFA also reduced by 45% and Total Bacteria Count to 10^3.
- After 2 months, we could bring the VFA to the desired levels of under 400. By then, the Total Bacteria Count slide also showed Nil growth

Case Study 3

Case study 3

Test Liner Paper Mill | Capacity - 300 TPD

Furnish – 100% recycled fiber

Location – Gujrat

	Blank	Day 2	Day 10	Day 30	Day 60
Chlorine Dioxide in Wet End	0 ppm	3 ppm	3 ppm	2 ppm	2 ppm
Biocide in Starch	100g/ Mt	150 g/ Mt	150 g/ Mt	100g / Mt	90g/ Mt
Biocide in Wet End	150g/ Mt	150g/ Mt	150g/ Mt	100g/ Mt	90g/ Mt
ORP (mV)	- 110	- 105	- 48	+ 20	+ 120
VFA (mg/ltr)	425	405	340	275	215
Bacteria Count	10^4	-	10^3	10^2	10^2

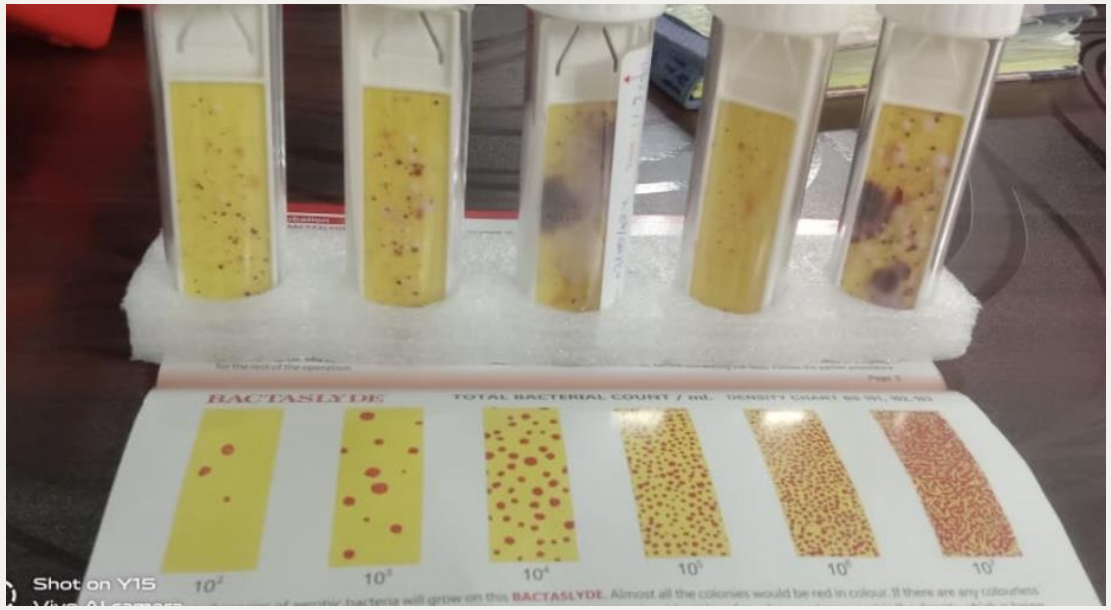
Prior to trials we conducted a hot alkaline wash of the Starch tanks and Size Press with our Oxidising Cleaner. (pH =9.5 Temp : 70C. Oxidising Cleaner : 1Kg per M3)

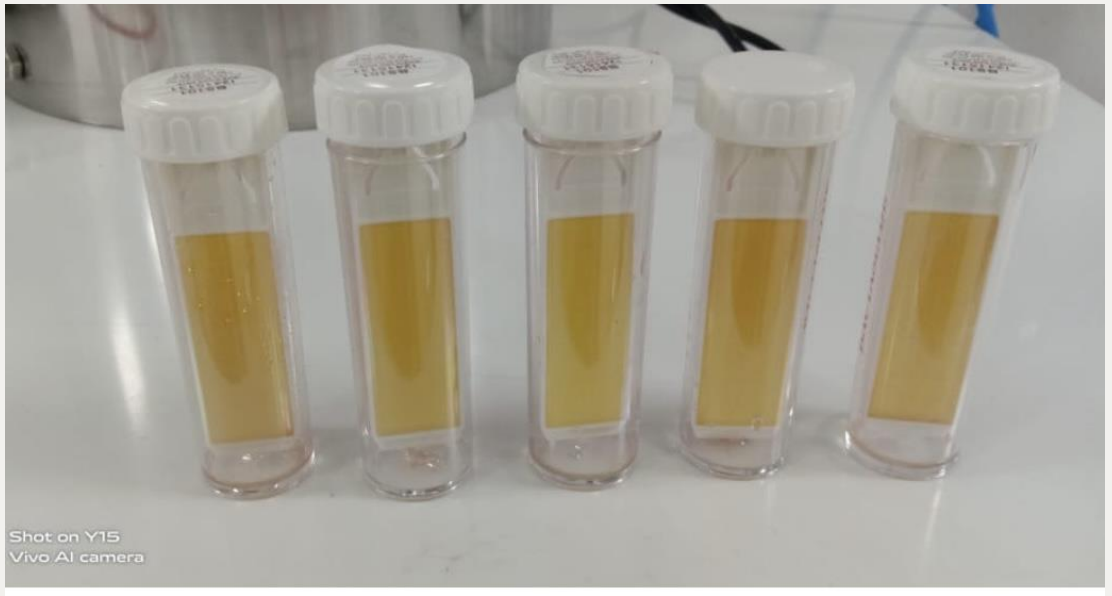
Case study 3

Test Liner Paper Mill | Capacity - 300 TPD

Furnish – 100% recycled fiber

Location – Gujrat





Results of Case Study 3

- In this Case, the Paper Mill was already using a Bio Control Program. Hence, the VFA was 425 mg/ltr but ORP was negative 110 to 140. Bacteria Count in the Head Box, Silo, as well as ETP water was 10^4 which showed that contamination was low but present.
- After incorporating our Bio Control Program, in the first week itself we observed that VFA was reducing slowly, and ORP was rising.
- In a month time, we were able to reduce VFA to below 300 and increase the ORP levels in the positive side. and Bacteria Count to 10^2.
- After 2 months, we could bring the VFA to the range of 200- 240 from 400-450. By then, the Bacteria Count slide also showed Nil contamination.
- Apart from this, there was a considerable cost reduction of about13% in their Bio Control Program.

Conclusion

Conclusion

In the course of our investigative research and through various plant trials, we found that the synergy of Chlorine dioxide and Non –oxidizing Biocide for Starch presents a promising solution for odour control in paper mills. Its effectiveness in controlling microbial growth and reducing odour-causing compounds makes it a valuable tool for improving the quality and environmental sustainability of paper production.

The application of **Biocides** in starch-based size press formulations plays a crucial role in reducing microbial-induced odor, while **Chlorine Dioxide** is highly effective as a biocide against bacteria, fungi, and algae commonly found in water systems in the papermaking process.

Along with above, Good housekeeping and Sanitation are essential to keep the system clean of deposits . These deposits are repositories of bacteria, mould and fungi. Hence starch tanks, size press and other vessels should be periodically cleaned with a hot alkaline solution containing an **Oxidising Cleaner.**

Thank You

Shiva Sharma

Director

Anmol Polymers Pvt. Ltd

IPPTA for giving us the opportunity to present our studies and to all the distinguished members present today.