

ANTIMICROBIAL TREATMENT, MONITORING AND CLEANING IN THE PULP AND PAPER INDUSTRY	Technical Leaflet TC CHAD, 1/2009
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Technical Committee on Chemical Additives (CHAD)
 Technical Subcommittee on Microbiology (FUA MB)
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1. Introduction

Microorganisms (bacteria, yeasts, fungi) are responsible for a multitude of problems in papermaking:

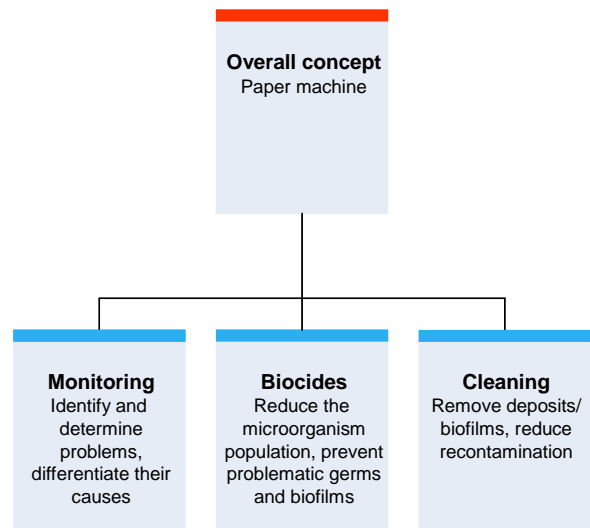
- Biofilms,
- Odours,
- Spoilage of raw materials and additives,
- Impaired machine runnability,
- Degraded product quality,
- Microbiologically induced corrosion,
- Foreshortened plant service life.

Accordingly, this technical leaflet addresses the entire trio of mutually interactive subject areas and clarifies the relationships between them. Some aspects can be considered independently of others, but an all-round understanding of mutual cause and effect is necessary for long-term success.

Microorganisms first get noticed when they induce detrimental effects. On the other hand, they take the blame for many difficulties even when there is no causal link. So in the interests of process stability throughout the production cycle, it is wise to identify microorganisms along with the consequences caused by their presence, and adopt countermeasures.

There are many approaches directed at putting a brake on the growth of microorganisms, or indeed eliminating them. Current practice focuses on biocidal and other antibacterial strategies, with active agents that are deployed preventatively against microorganisms. This tends to be seen as the one and only solution to the problem; yet experience shows there are more dimensions than that.

To begin with, it is absolutely essential to clean the paper machine and its peripherals: cleaning alleviates problems whose root cause is microbiological, and avoids a rapid resurgence in the microbe population. The second vital activity is monitoring: the problem has to be identified before countermeasures are adopted. Not every problem experienced with a paper machine will have a microbiological cause; monitoring provides a systematic means for detecting and sizing up issues.



2. Monitoring

In papermaking, monitoring is all about determining the microbiological state of a system. Monitoring helps to define, scrutinise and optimise general hygiene measures and should be considered as a means for avoiding microbial induced damage.

2.1 Material

The range of materials to monitor is diverse, and may be categorised into principal groups as follows:

- Fresh water
- Process water (white water, circulation water)
- Material systems (waste, thick stock)
- Dispersions (pigment slurries, coating colours, fillers, starch slurries)
- Emulsions (retention agents, thickeners, antifoaming agents)

2.2 Methods

2.2.1 Sample preparation

The type of material under investigation will determine how samples are prepared, and the choice of test method. Generally speaking, it should be noted that microorganisms tend to settle on surfaces, so solid matter must be taken into consideration.

2.2.2 List of methods

See **Table 1**.

2.2.3 Monitoring frequency

Just how often to perform the monitoring should be defined within a schedule framework. Factors to consider are the sensitivity of the material to be tested, and the requirements expected of the process flow and the product. Where applicable, the frequency of testing can be agreed in cooperation with the biocide supplier.

2.2.4 Economic aspects

A quantitative cost/benefit analysis of monitoring vs. consequences is difficult and depends on individual circumstances. Broadly speaking, the damage caused by microbial activity is frequently far more expensive than the cost of monitoring. This is true not only for the specific material at issue, but also for the final product and production plants generally.

Table 1: Summary of monitoring methods

Method	Evidence / Application	Advantages	Disadvantages	Level of training / experience	Time expenditure (incl. analysis)	Testing methods (DIN, EN, ISO)
Aerobic total germ count (TGC)	Exploratory appraisal of microbiological contamination (aerobes)	Simple and quick to perform	Unspecific evidence, time factor	Low	>2 days	-DIN 54379 (Apr 1992), -DIN EN ISO 6222 (Jul 1999) -ISO 8784-1 (1987) -ISO 8199
Anaerobic total germ count (TGC)	Exploratory appraisal of microbiological contamination (anaerobes)	Provides further evidence	Unspecific nature of the evidence; time and effort involved	Experience necessary	>3 days	
Sulphate-reducing bacteria (SRB)	Detection of cause of odour or corrosion	Simple	Time factor	Low	>3 days	-DIN EN 26461 part 2 (Apr 1993) / -ISO 6461-2
Yeasts / mould*	Direct detection of yeasts and moulds	Provides further evidence	Difficult to quantify; time factor	Experience necessary	5 days	-DIN 54378 (Apr 1993)
Catalase	Measure of microbial activity in the deinking process or in pigment slurries	Fast	Indirect, general	Low	10-15 min.	-Zellcheming Bulletin V/27.10/98
Redox potential	Indicator for retention times / assessment for application of oxidising biocides / trend recording	Fast; can be performed online	Unspecific	Low	5 min	-DIN 38404 part 6 -DEV C6
pH value	Indicator for retention times, heavy contamination and inorganic deposits / trend recording	Fast; can be performed online	Unspecific	Low	5 min	-DIN 53124 (Nov 1988) -DIN 38404 part 5 -DEV C5 -ISO 6588 (1981 mod.)
Oxygen loss (O ₂ loss)	Indicates heavy microbial contamination / trend recording	Fast; can be performed online	Unspecific	Low	5 min	-DIN EN 25814 -ISO 5814 -DEV G22
Adenosine triphosphate (ATP)	Measure of metabolic activity	Simple and quick	Error-prone; not universally applicable	Low	5 min	
Genetic probes	Specific detection or exclusion of particular microorganisms using fluorescence microscopy	Highly specific; fast	Major technical effort; cost-intensive	(Much) experience necessary	2 hours	
Microscopy	Exploratory preliminary investigation (morphology)	Simple, fast, specific	Major technical effort	Training and experience necessary	Variable, but fast as a rule	According to D.H. Eikelboom & H.J.J. van Buijsen
Biofilm monitoring	Checking for deposits	Distinguishes between continuous and discontinuous processes, to avoid process upsets	Equipment not freely available in the marketplace; lack of standardisation	Direct experience necessary	Variable, several weeks as a rule	
Dehydrogenase activity	Measure of microbial activity	Fast	Indirect, general	Low	>5 hours	
Odour monitoring	Exploratory preliminary investigation / quality control	Fast, sensitive	Subjective	Much experience necessary	Variable, but very fast as a rule	

* occur in the acid region

3. Cleaning

3.1 The need for cleaning

Deposits and soiling impair plant productivity (runnability) as well as the quality of the final product. Good plant hygiene not only improves machine availability, it also prolongs the plant's working life. And plants that are cleaned need less biocide.

3.2 How soiling and deposits occur

Deposits and soiling are basically chemical, physical or biological in nature (e.g. precipitation reactions, solubility behaviour due to temperature gradients, precipitation of extracellular polymer material). In practice, however, they mostly appear as a mixture of all three, such that it is not always easy to distinguish between the primary deposit and effects that arise subsequently, or to determine how they interact. Analysis of the deposits is helpful for deciding about a cleaning strategy on the one hand, and on the other hand analysis findings can also help to prevent further deposits from forming in future.

3.3 Deposit removal

Cleaning is performed by the application of a washing liquor (with or without added cleansing chemicals) using specific techniques, all within defined parameters. The cleansing agent(s) deployed will depend on the type of deposit to be tackled:

- Acid (mineral and organic acids, surfactants),
- Alkaline (caustic chemicals, complexing agents, surfactants),
- Neutral (surfactants),
- Organic solvents.

Dispersants are also used to assist the cleaning process and prevent the deposits from re-forming.

The application techniques below are used industrially, either with or without chemical additives:

- Mechanical,
- High-pressure,
- Low-pressure,
- Foam cleaning,
- Circulating wash liquor,
- (Dis)continuously through a shower jet.

Exposure time, temperature, pH value and the choice of cleansing chemicals are all key factors in successful cleaning. For cleaning efficiency, these parameters need to be adjusted on a case-by-case basis in consultation with the supplier of the chemicals.

Acidic and alkaline cleansers will be chemically consumed to some degree while in use. So to maintain an adequate cleansing effect it is advisable to check the acidity or alkalinity, and post-dose cleansing agents accordingly. High temperatures tend to assist the cleaning process.

Table 2 presents a summary of techniques for removing deposits.

Table 2: Summary of techniques for removing deposits

Location	Type of deposit	Technique	Cleansing agent	Remarks
Stock/pulp system	Resinates	Alkaline wash liquor, followed by high-pressure mechanical cleaning	Caustic soda and tensides, possibly in the form of foam cleanser	pH value must be maintained at >13 for several hours
Stock system	ASA	Acidic wash liquor	Acids and organic solvents	pH between 2.5 and 3
Stock system	AKD	Alkaline wash liquor	Caustic soda / caustic potash	Adding organic solvents boosts effectiveness
Stock system	Slime	Mechanical, followed by alkaline wash liquor	Caustic soda and tensides	pH value should be maintained at >13 for several hours
Stock system	Calcium carbonate, magnesium carbonate	Acidic wash liquor, foam cleansing	Phosphoric acid, sulphamic acid	
Stock system	Calcium oxalate	Alkaline wash liquor	Alkaline, plus complexing agents	
Stock system	Stickies	Wash liquor	Aromatic solvent	
Starch system	(Retrograded) starch	Alkaline wash liquor, foam cleansing	Caustic soda and tensides, possibly amylases	
Stock system	Aluminium oxide	Alkaline wash liquor, foam cleansing	Caustic soda	pH value must be >10
Storage tanks	Binder residues	Alkaline foam cleansing, mechanical	Alkaline foam cleanser	
Storage tanks	Pigment sediments	Mechanical, high-pressure		Chemicals are not absolutely necessary
Drying cylinder	Resins	Organic solvents, possibly alkaline aqueous as well	Cold cleaning solvent, or possibly alkaline foam cleanser	Use a high boiling-point solvent to prevent evaporation

4. Antimicrobial treatment

The biocides used may be monoproductions (containing just one active agent), or else combination products (containing multiple active agents) – this expands the spectrum of efficacy and the application possibilities. Dispersants can improve the biocides' effectiveness.

Systemic conditions may impair the effectiveness of biocides: these include pH (strongly acid or alkaline), temperature (below 10°C, above 50°C), high COD values (> 5.000 mg/l), reductive conditions, or residual sulphites (with oxidative biocides) and chemical incompatibilities.

There exists a possibility of biocides having a detrimental effect on the papermaking process (foaming problems, colour space shift, precipitates), so issues like these should be tested for ahead of application. It is important that the biocide system is precisely matched to the individual requirements arising from problems with the respective paper machine and material/water circuits.

Laboratory trials can be used to test biocides for their suitability in a given application. Testing techniques, usually involving classical microbiological methods, provide valuable pointers to biocide treatment in practice.

Field checks and monitoring are required when biocide is applied. Systemic changes can be tracked using online methods, while classical microbial detection methods serve to ascertain a general microbiological status and to discover specific microorganisms whose presence is problematic to storing raw materials and additives.

The sale and application of biocides is subject to specific statutory principles and conditions: the 98/8/EC Biocides Directive, REACH, the 36th recommendation of the German Federal Institute for Risk Assessment (BfR), environmental labels (EU Flower, Nordic Swan, Blue Angel), environmental and safety aspects.

Tables 3-5 presents further details about antimicrobial treatments.

Table 3: Biocide application

Dosage	Characteristic	Application	Dosing intervals
Continuous	Steady biocide dosing throughout the daily period	Fresh water	Daily, usually below 10ppm
Discontinuous	High biocide dosage over a brief period (dosing peaks), such as to exceed of the threshold value that will effectively kill off the microorganisms	Primary and secondary circuit, thick stock area, additives	4-12 doses per 24-hour period; concentrations during dosing peaks reach 5-50 ppm in the water circuit and 30-150 ppm with additives
Single-dose	Produces a high concentration of biocide	Filling of pigment storage tanks	Once only, 150-300 ppm

Table 4: Biocide treatment objectives

Application	Treatment objective
Fresh water (FW)	<ul style="list-style-type: none"> Fast and effective sterilisation Stopping algae
Primary and secondary water circuit	<ul style="list-style-type: none"> Delaying biofilm formation, levelling to a film thickness that is unproblematic Stabilisation of germ counts, cutting down the population of problematic germs in particular (hygiene germs, slime-forming microorganisms, filamentous bacteria and others) Preventing microbiological infestation of material
Thick stock area	<ul style="list-style-type: none"> Medium-term prevention of biologically-caused degradation, avoidance of strongly anaerobic conditions Germ count stabilisation Cutting down the population of problematic germs (anaerobic microorganisms, slime-forming bacteria, and others)
Raw materials and additives	<ul style="list-style-type: none"> Medium- to long-term prevention of biological infestation, especially by anaerobes Effective diminution of germ levels Stabilising a low germ level
Finished product	<ul style="list-style-type: none"> Prevention of microbiologically-induced quality impairments

Table 5: Active agents and their principal applications

Class	Examples	Principal application
Oxidising biocides	Peroxyethanoic acid	Process water, fresh water
	Hydrogen peroxide	Process water
Oxidising, halogenated	Halogen alkyl hydantoins, BCDMH, DCDMH, MCDMH	Process water, fresh water
	Hypochlorite, hypobromite, chlordioxide	Fresh water
	Hydantoin method	Process water, fresh water
Surfactant compounds, with simultaneous prevention of deposits	Quaternary ammonium compounds	Process water
	THPS	
Bromine-nitrogen compounds	DBNPA	Process water, material systems, emulsions, dispersions
	Bronopol (BNPD)	Material systems, emulsions, dispersions
Cyanates	MBT	Material systems, emulsions, dispersions
Thiocarbamates	Carbamate	Material systems, emulsions, dispersions
Isothiazolins	CMIT:MIT	Material systems, emulsions, dispersions
	BIT	
Aldehydes	GDA, Formaldehyde releasers, hemiacetals	Process water, material systems, emulsions, dispersions
Cyclic compounds	o-phenylphenol (OPP)	Material systems, emulsions, dispersions
In-situ compounds	Ammonium bromide technique	Process water
	Ammonium sulphate technique	