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# Case Histories: Biocide Interactions and Development of Microbial Tolerance/Resistance to Biocides in the Paper Making Process

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## HEALTH and SAFETY

- Worker Exposure
  - **Carcinogenicity**
    - Formaldehyde
  - **Toxicity**
    - Spills: Bucket Brigade, Totes
    - Leaks: Pumps, Lines, etc
  - **Corrosiveness**
    - Burns (Boots)
  - **Lachrymation/ Irritation**
  - **Sensitization**
    - Paper Mill employees (isothiazolin, neat chemical)
  - **Chemical Fumes**
    - MITC (Paper customer's customer)
    - Formaldehyde
    - Glutaraldehyde

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# BIOCIDES ADDITION

- **Addition / Mixing**
  - Addition to top of slurry
  - Injection into outlet side of recirculation pump
  - Inadequate mixing
    - Improper blade type/size
    - Inadequate rpm
    - Improper baffle design
    - Improper tank design
    - Absence of recirculation system
- **Flocculation**
  - pH
  - Non-uniform distribution
    - Untreated slurry
  - Inadequate biocide/pigment contact



# BIOCIDE CHEMICAL/ENVIRONMENT INCOMPATIBILITY

- **Biocide – Biocide**
  - Thione incompatible with
    - Glutaraldehyde
    - Isothiazolin
    - Benzisothiazolin
- **Biocide – Chemical**
  - pH (alkaline – isothiazolin, glutaraldehyde)
  - Temperature
  - Dye
  - Protein (primary amines)
  - Ammonia (other primary amines)
  - Reductants (bisulfite, hydrosulfite)
  - Oxidants
    - H<sub>2</sub>O<sub>2</sub>
    - Hypochlorite
    - Chlorine
    - Chlorine dioxide



# DEVELOPMENT OF TOLERANCE/RESISTANCE TO BIOCIDES (initially effective)

- **Definition**
  - Tolerance
  - Resistance
- **Causes**
  - Biofilm (inadequate housekeeping)
  - Use of minimal level of biocide(s)
  - Use of single biocide
- **Prevention**
  - Dual biocide or biocide/oxidant programs
  - Alternating biocide programs
  - Housekeeping
- **Examples**
  - Benzisothiazolin (Screen blinding – e.g, DTBBA)
  - Glutaraldehyde (Valerolactone)
  - Isothiazolin
  - Hydrogen peroxide (Catalase - all aerobic organisms)
  - Sodium ortho phenyl phenate
  - Bromonitropropanediol



# MAINTENANCE OF MICROBIOLOGICAL CONTROL

- **Frequency (typically inadequate)**
  - Exponential growth (don't wait until TNTC to treat)
- **Sampling (typically improper)**
  - Representative
  - Contamination
    - Sampling site
    - Sampling container
- **Testing**
  - Microbial
    - Procedures
    - Microbial “specs”
    - “Challenge” testing
  - Chemical
- **KEY Simultaneous microbial and chemical testing are critical for making treatment decisions.**



# COATING PROCESSES

- **Coating Preparation**
  - **MB quality of individual components**
    - Knowledge of what biocide(s) the supplier is using (FDA, compatibility)
    - Clay/Carbonate/TiO<sub>2</sub> pigments
    - Latex
    - Starch (butyric acid)
    - Protein
    - Water based dyes
    - CMC (other stabilizers)
- **Intermediate Coating Storage**
- **Coating**
  - Recycled to/from coater run tanks
  - Dead headed to coater run tanks
- **Coater Run Tanks**
  - Recycled coating (contaminated)
- **Housekeeping / Biofilm (typical source of tolerant/resistant microbes)**
- **Water Quality**
- **Closed water systems**
- **Recovery of Spoiled Coating**
  - Odor
  - Color
  - Viscosity





# SUMMARY

- **Paper Mill – Supplier relationship**
  - **Agreement**
    - Biocides (type, level, regulatory)
    - Microbial and biocide levels when vessel is unloaded
    - Biocide(s) in incoming slurry will not control microbes subsequent to vessel
- **Paper Mill**
  - **Housekeeping**
    - Unloading and storage systems (clean frequently)
    - Preventing biofilm formation (recontamination, tolerance/resistance development)
  - **MB control (stored raw materials)**
    - Frequent sampling / testing for microbes and biocides
    - Safe handling
    - Facilitate biocide addition and mixing
  - **Coating**
    - Raw material MB control
    - Biocide addition to coating / coating storage time
    - Housekeeping
    - Recycled coating MB control
  - **Water quality**

