Controlled Release Antifouling Coatings

Paul Kappock
Arch Chemicals, USA
Why Need for Antifouling Coating?

- Increased speed
- Fuel savings (50% of operating costs)
  - 40% less fuel used on clean hull
- Reduced pollution (less fuel)
- Repair costs (engines work less)
- Ship appearance
- Transmigration of organisms
- Overall as much as $10 billion saved per year
Why Need for Controlled Release?

• Paint film will be “active” longer
  – Biocide will leach out for years
  – Up to 5 years of protection

• Minimize impact on environment
  – Only enough biocide released as necessary
  – Adjust (formulate) release rate for boat operating conditions
Evolution of Coatings

- **Old technology**
  - Insoluble binder, soluble biocides
  - Biocides leach out, leaving very porous film
    - Porous film creates drag, fouls quickly
  - High initial leach rate
    - Wasted biocide
  - Slow leach rate when old
    - Loses efficacy
    - Must use more biocide due to variable leach rate
Evolution of Coatings

• Newer technology
  – Ablative polymer (Controlled depletion polymer)
    • Slightly water soluble (alkaline) binder
      – Usually Rosin or polyvinyl methyl ether and vinyl chloride
    • Film slowly dissolves away, becomes rougher over time
    • Relative large leach layer
      – Biocide diffusion from film, high when fresh
      – Formation of leach layer of insoluble materials on surface
        » Becomes thicker over time
      – Lower biocide concentration at surface, biocide release rate and binder dissolution declining with time
    • Use more biocide due to variable leach rate
    • Must remove leach layer prior to recoating
    • Used in lower fouling areas or frequent painting intervals
Evolution of Coatings

- Newer technology
  - Self polishing Copolymer (SPC)
    - Reactive pendant group
    - Surface of film hydrolyzes in seawater, becoming water soluble
      - Layer of water soluble polymer wears off
    - Thinner leach layer
      - More constant biocide release rate
  - Surface becomes smoother than when first applied
  - Recoating requires less preparation than Ablative type coating
    - Leach layer thinner and easier to remove
  - Generally use less biocide with better and longer performance
  - Cost more than Controlled Depletion Polymer (CDP) paints
Amount depleted

Leached Layer = 75 μm

CDP Cross-Section
Amount polished off

Leached Layer ~ 10 μm

Acrylate SPC Cross-section
Typical Leached Layer of CDP
Hybrid Coatings

- Use both rosin and SPC
- Leach layer intermediate between CDP and SPC
- Cost and performance also intermediate
Biocides for Antifouling

• **Primary Biocide**
  - Hard Fouling (Barnacles, Mussels)
    » Cuprous oxide, Copper Thiocyanate, Copper metal
    » Triphenyl Borons (pyridine triphenyl boron)

• **Booster Biocide**
  - Soft Fouling (Algae)
    » Pyrithiones
    » Thiocarbamates
    » Triazines
    » Isothiazalones
Self Polishing Copolymers (SPC)

• Silyl Acrylate
• Copper Acrylate
• Zinc Acrylate

Hydrolysis followed by loss of solubilized layer of polymer

Paint Film becomes smoother with dissolution of film surface

Hydrolyzable monomer up to 50 mole % of copolymer
Cap Hydrolysis in Seawater to form acids, then carboxylates

Self Polishing

+ Cap byproducts (Biocides)
Hypothetical Zn Acrylate

R = H, Me
R₁ = alkyl and R₂ = alkyl
Hypothetical Silyl Acrylate

\[ \text{CO}_2\text{R}_1 \quad \text{R} \quad \text{Si} \quad \text{R}_2 \]

\[ \text{R} = \text{H, Me} \]

\[ \text{R}_1 = \text{Alkyl} \]

\[ \text{R}_2 = \text{t-butyl, isopropyl} \]
Self Polishing Copolymers (SPC)

Polishing rate determine by

• Pendant groups
  – Hydrophillic (acrylic acid)
  – Hydrophobic (butyl acrylate)
• Mole % of hydrolysable cap monomer
• Hydrolysis rate of cap monomer
  – Structure of cap monomer
• Molecular weight of polymer
• Crosslinking and chain entanglement
• Paint formulation (amount and type of pigments)
Biocide Release from SPC

• Cuprous Oxide
  – Low solubility in sea water (5 ppm at pH 8.2)
  – Solubilized and slowly released from leach layer

• Pyridine triphenyl boron
  – Hydrolysis in sea water

• Organometalics
  – Pyrithiones (Zn and Cu)
  – Thiocarbamates (Ziram, Zineb)
  – Very low water solubility (0.1-8 ppm)
    • Very slowly released from leach layer
  – Leach rate for above dependent on polymer polishing rate, and water solubility
Biocide Release from SPC

• **Organics**
  - **Triazines** (2-methylthio-4-tertbutylamino-6-cyclopropylamino-s-triazine)
  - **Isothiazalones** (4,5 dichloro-2-n-octyl-4-isothiazalone)
  - **Dichlofluanid**
  - **Tolylfluanid**
    - Very Low water solubility (1-8 ppm)
    - Miscible in polymer
      - Possible to plasticize polymer
      - Biocide migration possible
    - Biocide leach rate dependent on polishing rate, miscibility in polymer, and water solubility
SPC Paint Efficacy

• Combination of
  – Polishing rate of polymer
    • Expressed in µm/mo.
  – Leach rate of Biocides
    • Expressed in µg/cm²/day
  – Toxicity of biocides toward target organisms
  – Coating film thickness. Thicker lasts longer
    • 200 µm film with 4 µm/mo polish rate lasts 50 months

• Ships operate differently
  – Oil Tankers always on the move
    • Require lower polishing rate
  – Military ships may dock 50% of the time
    • Require higher polishing rate

• For Cu2O, leach rate must be at least 10 µg/cm²/day for any type of ship
SPC Paint Efficacy

- Minimal amount of biocide delivered at a constant rate to reduce waste
  - Delivered at high enough rate to be toxic
  - More toxic biocides are delivered at a lower rate
  - Difficult for polymer miscible biocides to release at constant rate
- Ideal for biocide front and polymer front to move at same rate
  - Need more toxic biocide for slow polishing polymer or higher amount of less toxic biocide
    - Limit to how much biocide is practical
  - Faster polishing polymer could use less toxic biocide or less of more toxic biocide
Average hull Roughness

- Maximum smoothness = maximum efficiency
- Measured in µm as maximum peak to trough height over 50 mm of surface
  - All reading then averaged
- Wavelength also important measure of hull smoothness
- Self polishing copolymer antifouling paints become smoother (polish) over time
Average Hull Roughness

0--------------------------------------------------------50mm

125μ

100μ

0--------------------------------------------------------50mm
Summary

• Trends are
  – Away from more toxic biocides
  – Away from environmentally persistent biocides
  – High metal content (copper)
  – Foul release (no biocide)

• Controlled release (SPC) allows
  – Less toxic biocides
  – Lower amounts of biocide
  – Favorable cost/performance
Acknowledgements

• Colin Anderson, International Paint website for leach layer photos

• Gary Silverman and Mark Aubart of Arkema, Inc. for SPC hydrolysis mechanism