Controlled Release Antifouling Coatings

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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

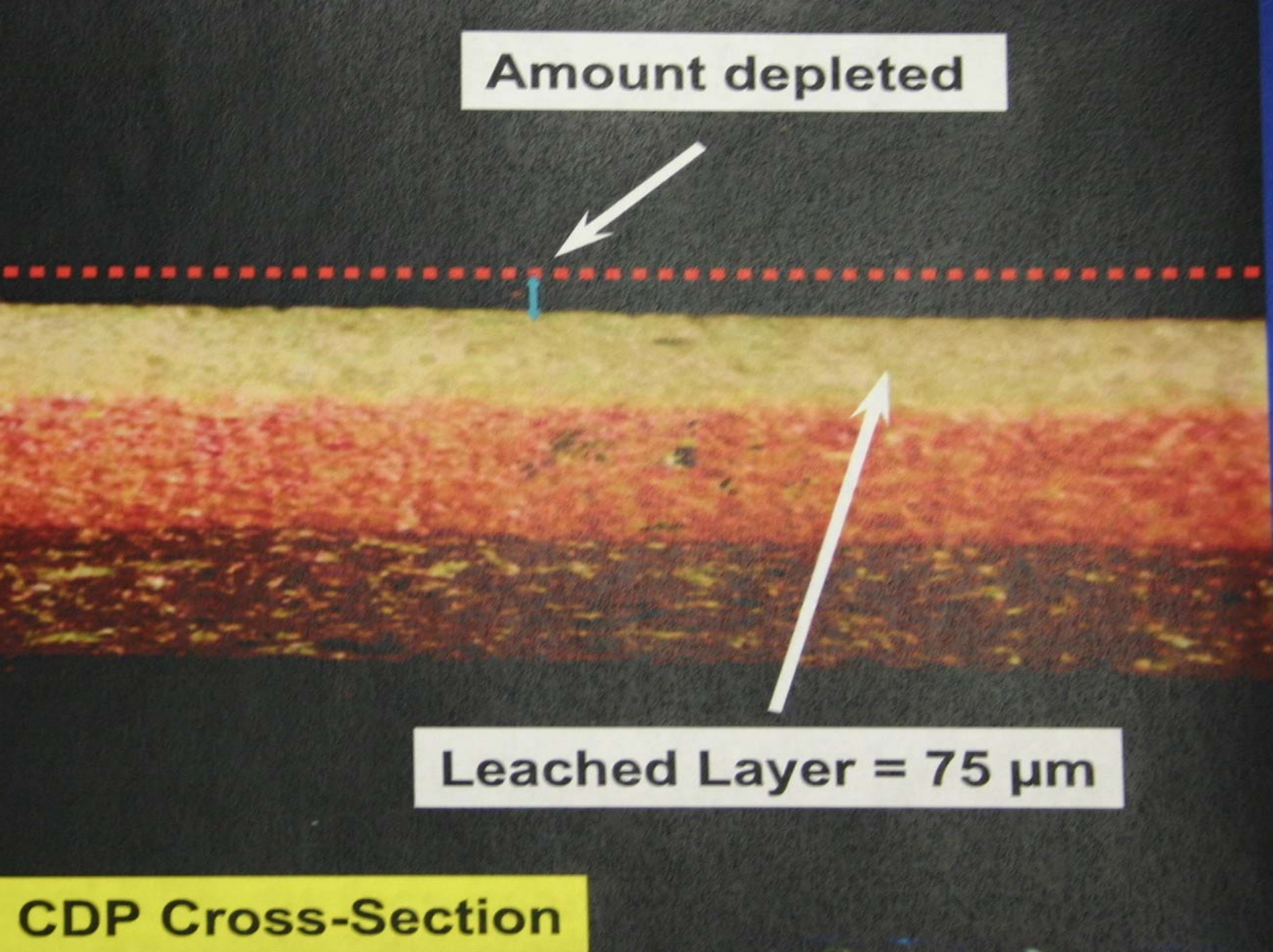
- Old technology
  - Insoluble binder, soluble biocides
  - Biocides leach out, leaving very porous film
    - Porous film creates drag, fouls quickly
  - High initial leach rate
    - Wasted biocide
  - Slow leach rate when old
    - Loses efficacy
  - Must use more biocide due to variable leach rate

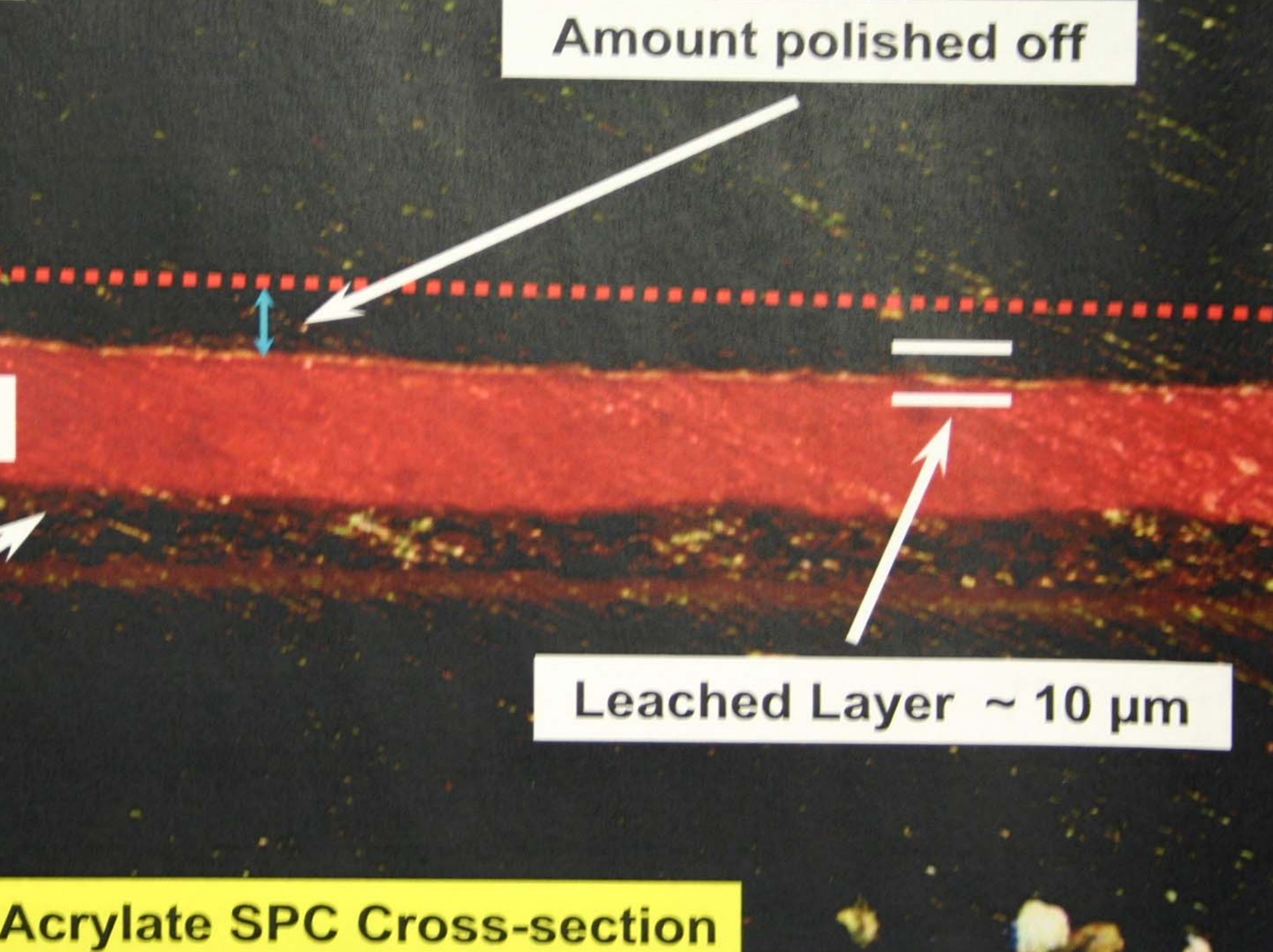
Evolution of Coatings

- 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

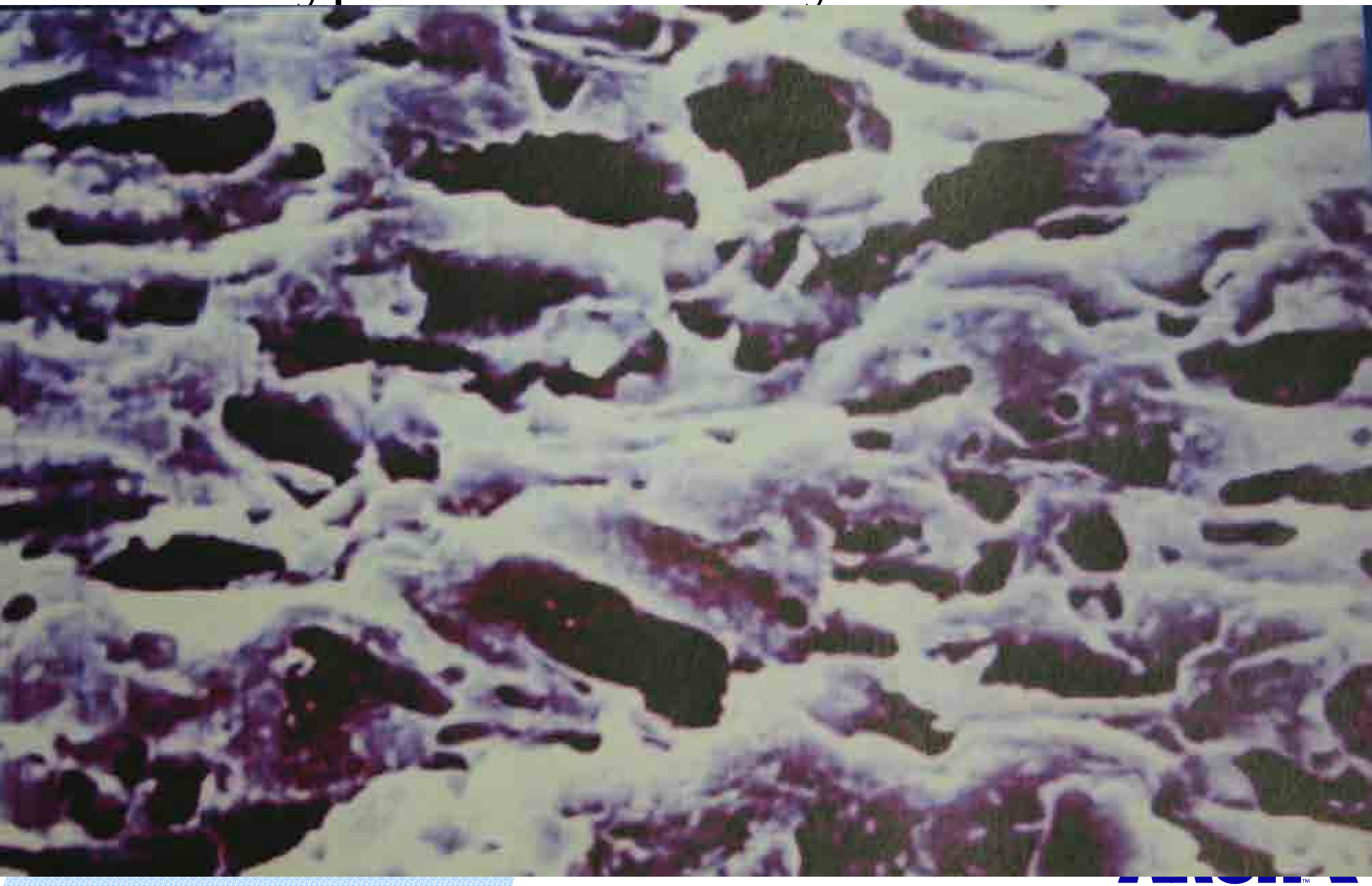
- Newer technology
  - Self polishing Copolymer (SPC)
    - Reactive pendant group
    - Surface of film hydrolyzes in seawater, becoming water soluble
      - Layer of water soluble polymer wears off
    - Thinner leach layer
      - More constant biocide release rate
    - Surface becomes smoother 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



Acrylate SPC Cross-section

Typical Leached Layer of CDP

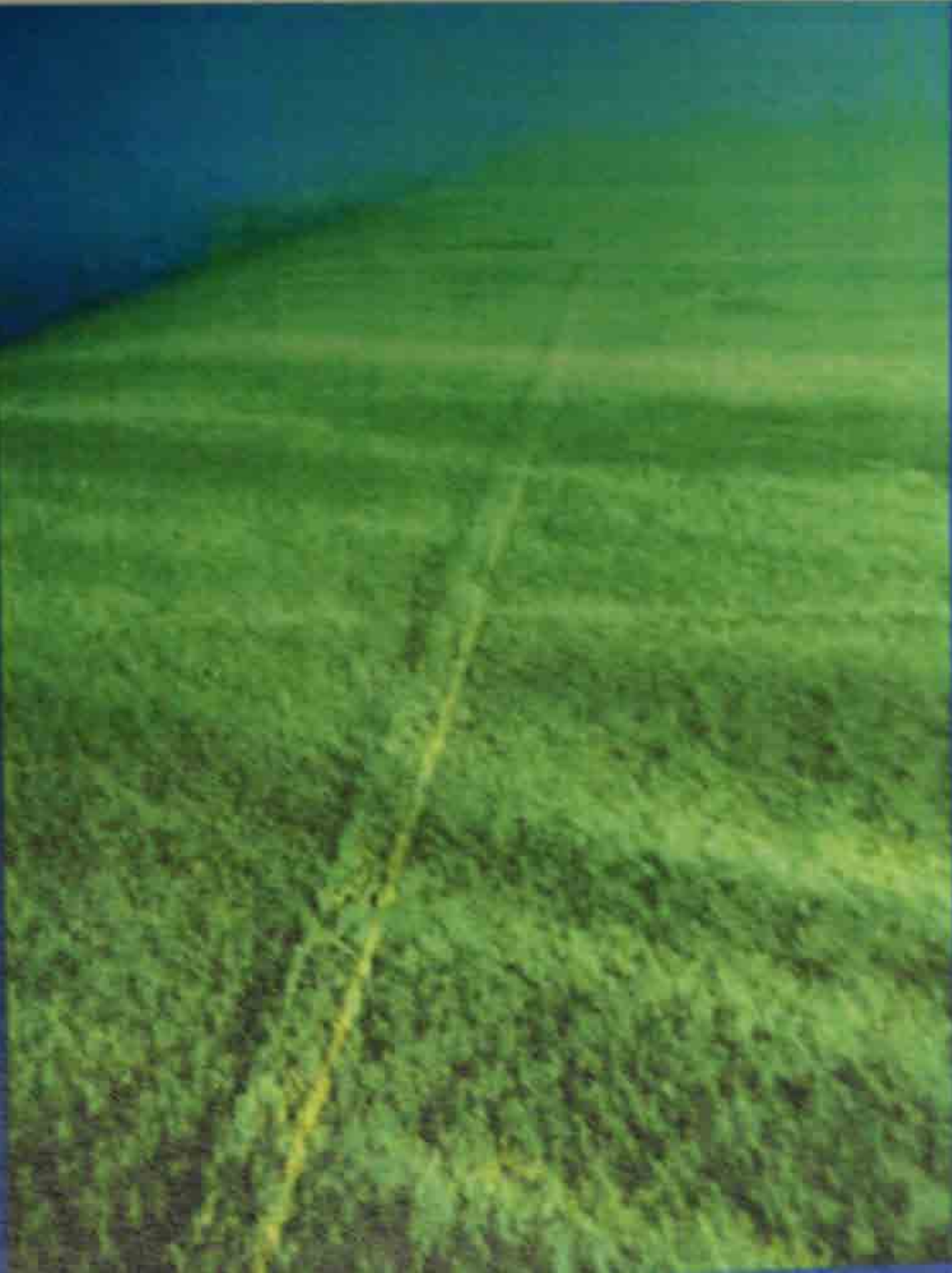


Hybrid Coatings

- 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



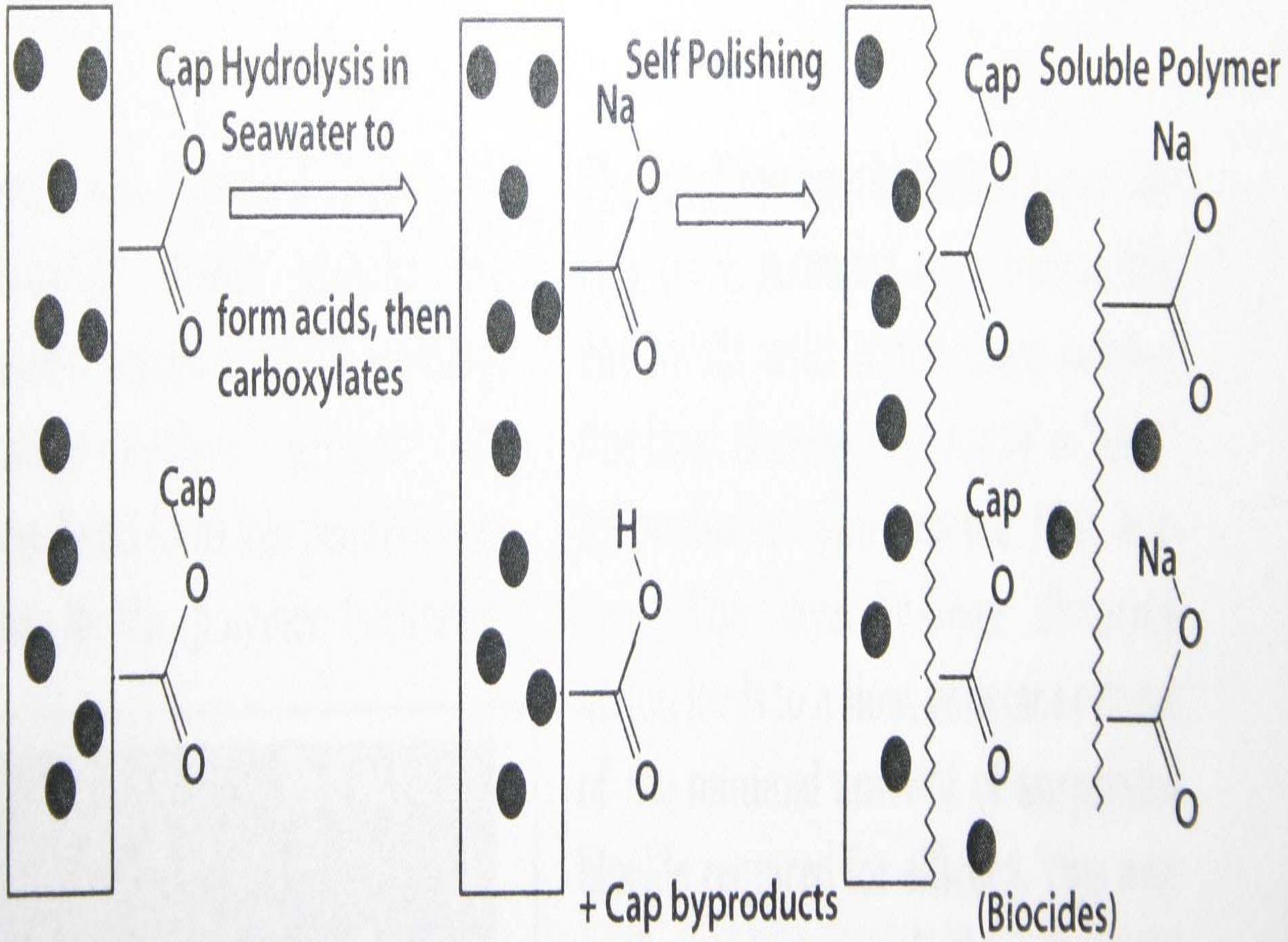
Self Polishing Copolymers (SPC)

- Silyl Acrylate
- Copper Acrylate
- Zinc Acrylate

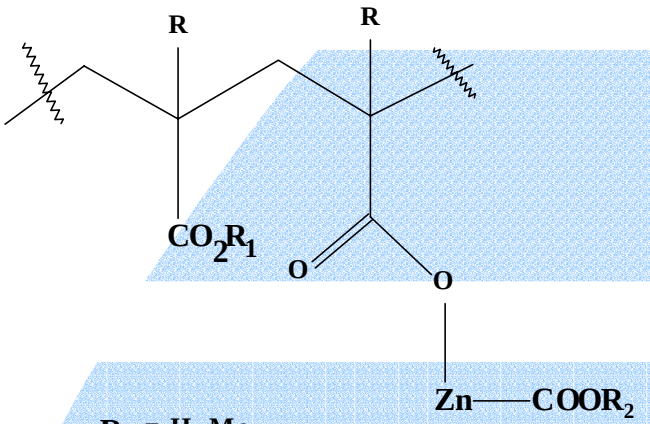
Hydrolysis followed by loss of solubilized layer of polymer

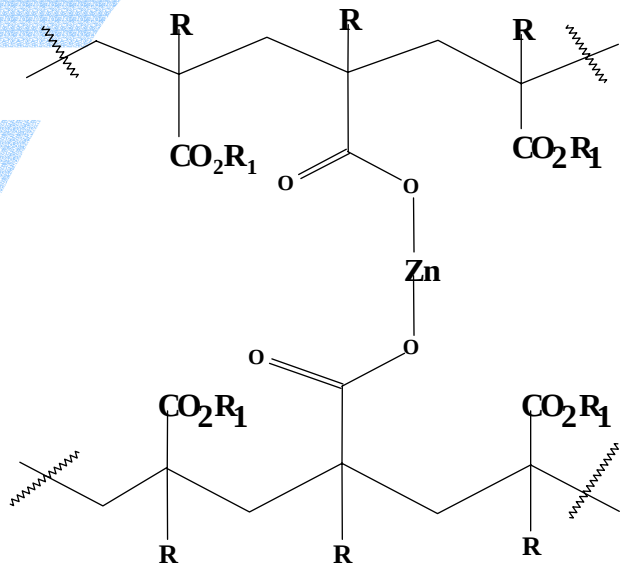
Paint Film becomes smoother with dissolution of film surface

Hydrolyzable monomer up to 50 mole % of copolymer


Cap Hydrolysis in Seawater to form acids, then carboxylates
Cap
O
O
Self Polishing
Na
O
O
H
O
O
+ Cap byproducts
Cap Soluble Polymer
Cap
O
O
Na
O
O
Cap
O
O
Na
O
O
(Biocides)

Hypothetical Zn Acrylate

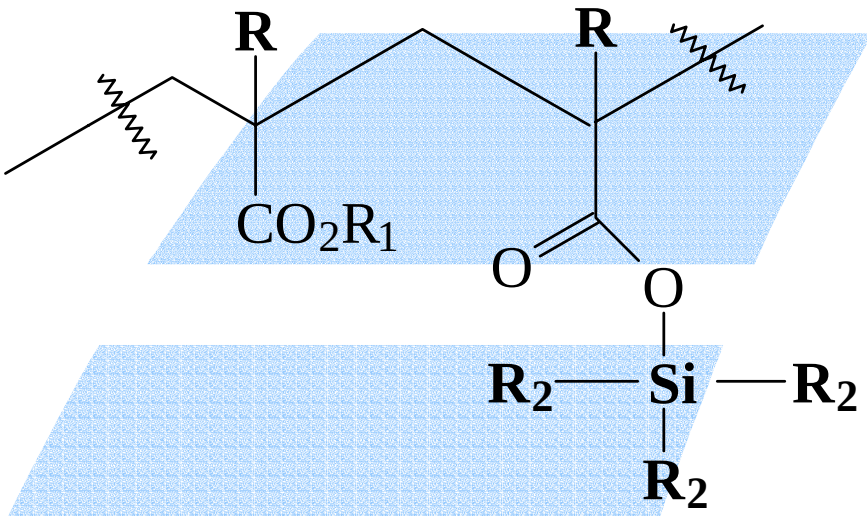




R = H, Me

R_1 = alkyl and **R_2** = alkyl

Hypothetical Silyl Acrylate



R = H , Me

R_1 = Alkyl

R_2 = *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
  - Pyrithones (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/cm^2/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/cm^2/day for any type of ship**

SPC Paint Efficacy

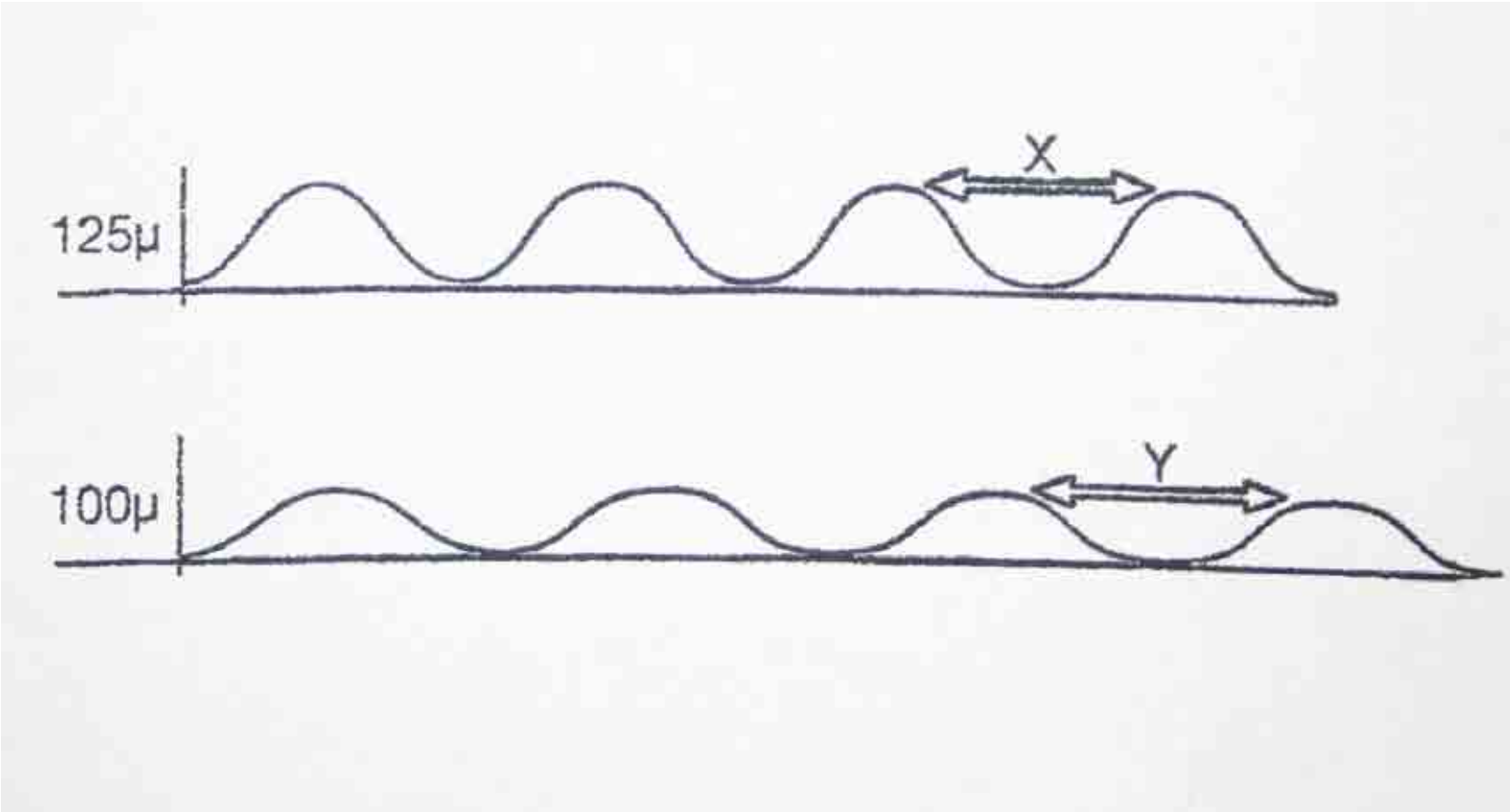
- **Minimal amount of biocide delivered at a constant rate to reduce waste**
  - **Delivered at high enough rate to be toxic**
  - **More toxic biocides are delivered at a lower rate**
  - **Difficult for polymer miscible biocides to release at constant rate**
- **Ideal for biocide front and polymer 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

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, Internationl Paint website for leach layer photos

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