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Development of Corrosion Resistant Energy Curable Coatings

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Are there still opportunities for new paints?


Six cadets from the U.S. Coast Guard Academy were injured this month after slipping on a wave-soaked deck aboard their training ship in heavy seas about 300 miles off the coast of Newfoundland.

Five of the cadets were taken to a hospital in St. John's, the province's capital, with fractures and lacerations after the 70-year-old sailing ship, the *Eagle*, finally docked there. The sixth cadet had a sprained ankle and did not need hospital treatment. No injuries were life-threatening.

The *Eagle* was five days out of the academy, in New London, Conn., when it encountered rough seas in the North Atlantic. The injured cadets were treated aboard the ship. ➤

—KAREN BIRCHARD

➤ = Read more at http://chronicle.com/extras

- "Anybody ever had the paint on their back yard deck (or their house) peal?"
- *Non-slip deck coatings*
- Repair coatings
- Rapidly drying paints
- Antifoulants - friction reduction on ocean going vessels

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About …coatings & *paint*?!

- Paint - How dost thou dry/cure?

  - Oil based (ancient) oxidative/evaporative cure
  - Solvent born (acrylic)(post war) evaporative
  - Latex (H_2O) (post war) coalescence/evaporative
  - 2 part Epoxies/urethanes (1960's) - chemical reactions

Epoxide + diamine ---> condensed poly(ether)
Reaction is slow, the components and the solvents smelly,
But… the products are hard and stick voraciously to surfaces

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Photochemical (radiation/energy) cure - fast, can be turned on/off, imaged!

- Formulations of acrylates or epoxides + photoinitiators + light = rapid conversion of liquids to solids
- Large business already but little penetration in the large volume paint market (automotive, ships, airplanes, etc.)
- Commercial cure is with high intensity Hg (UV) or Xe (broad spectrum) light sources.
- Commercial systems that are 'in place' - move the sample and keep the energizing light stationary.
- Problem - how does one "paint" something that isn't flat?
- Opportunity - portable light sources.

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Radiation cure principles

Poly(acrylates) - wide variety photopolymers produce variety of final properties. Polymerize quickly. Multiple uses (90+%) of market

Poly(epoxides) - highly versatile - provide conformal control but polymerize slowly - dental fillings, prosthetic devices, stereolithograms as hybrids (up to 10% of market).

Additives - control color, adhesion, corrosion protection, and other properties important issues.

Basically one can engineer most final properties in virtually any photopolymerization system.

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Photochemical cure without light

- Materials and formulations that can be photopolymerized sell about $25 bil/yr.
- Said formulations are used as paints, coatings, varnishes, adhesives, claddings
- Problem - *what happens if light cannot get to a place that needs to photopolymerized?*

➢ **Remote Cure** - using airborn catalysts to cause a "photopolymerization"

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A real live submarine

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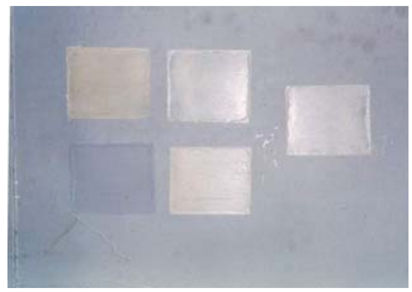
Inside a ballast tank

Submarine test samples

- Film forming monomers (30-75%)
- Fillers (corrosion inhibitors,extenders, plasticizers, 25 - 70%)
- Photoinitiators (2-4%)
- Amine coinitiators (3-10%)
- Additives (1-4%)



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The test process on SSBN 731

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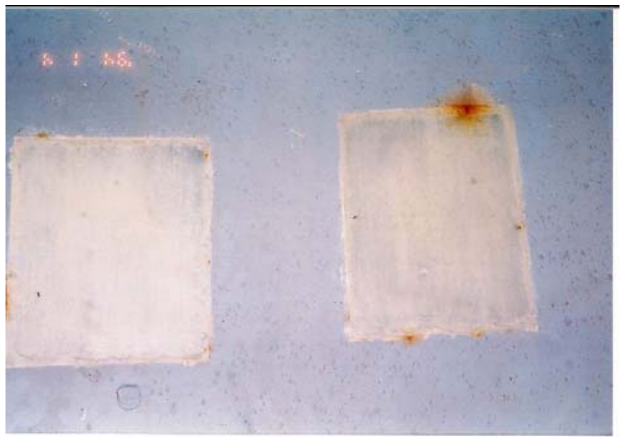
After 33 months



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Radiation cured paints

- Navy protocol approved
- Testing underway - formulations stable for 3+ years - ballast tank applications
- That means that they stick, they don't peel, they don't corrode, -- they compare/exceed 2 part epoxies in performance

What does it take for these paints to be adopted by the Navy/commercially?

1) Portable light source.
2) Procedure to paint in dark areas
3) Do it the way the Navy does! Sink 'em. nih (not invented here) that is!
4) A blue moon?

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Advantages/Disadvantages Radiation Cure

- Advantages
  - Fast
  - Versatile, high volume applications
  - Few personnel required.
  - Solventless - all solids
  - Can be imaged
  - Turnon/turnoff

    Light --> polymer

    Dark ---> no polymer
- Disadvantages
  - *High speed requires high light intensity/high power requirements.*
  - *Light/systems usually stationery.*
  - *Can't cure where light can't go.*
  - Properties
    - Speed may lead to shrinkage/brittleness
    - Adhesion to surfaces may be an issue.

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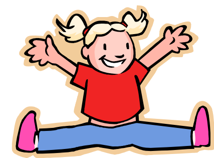
Our approach

- Work on those things we can do something about
  - Find/identify and collaborate with manufacturers of portable light sources.
  - Work with industry collaborators (nih functions in industry too, as well as in the Navy)
  - Undertake the challenges of remote cure - *photopolymerization without light* - the current project

Principles - If you can coat it, how can you cure … to



- Polymerize quickly forming hard?
- Coatings that contain anti-corrosives, anti-foulants, pigments?
- Polymerize only on command?
- Be non-toxic, non-polluting?

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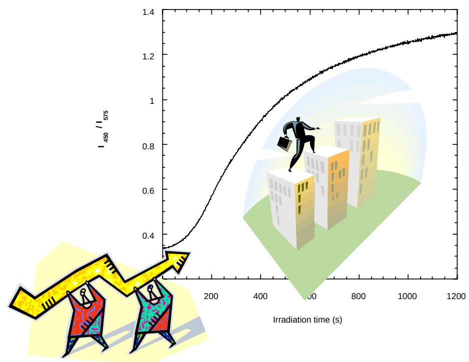


Formation of the radicals from R_3B

Mechanisms Proposed

Mechanism **A**

$R_3B + O_2 \longrightarrow R_2B\text{-}O\text{-}O\bullet + R\bullet$

$R\bullet + O_2 \longrightarrow R\text{-}O\text{-}O\bullet$

$R\text{-}O\text{-}O\bullet + R_3B \longrightarrow R_2B\text{-}O\text{-}O\text{-}R + R\bullet$

$R_2B\text{-}O\text{-}O\text{-}R \longrightarrow R_2B\text{-}O\bullet + RO\bullet$

H.C.Brown, M.M.Midland *Chem.Commun.* **1971**, 699

Mechanism **B**

$R_3B + O_2 \longrightarrow R_2B\text{-}O\text{-}O\text{-}R$

$R_2B\text{-}O\text{-}O\text{-}R \longrightarrow R_2B\text{-}O\bullet + RO\bullet$

F.J.Welch *J. Polym. Sci.* **1962**, *61*, 243-252

The system

- Most test systems contain a single acrylate monomer chosen from a variety of polyol(acrylates) used in coatings applications. System identical to those routinely cured photochemically.
- System contains one of several complexes the characteristics of which are still be investigated.
- Polymerization triggered by exposure to one of several gases.
- Polymerization followed spectroscopically using an *in situ* fluorophore to monitor cure (Jager, W. F.; Lungu, A.; Chen, D. Y.; Neckers, D. C. Photopolymerization of Polyfunctional Acrylates and Methacrylate Mixtures: Characterization of Polymeric Networks by a Combination of Fluorescence Spectroscopy and Solid State Nuclear Magnetic Resonance. *Macromolecules* **1997**, *30*, 780-791.)

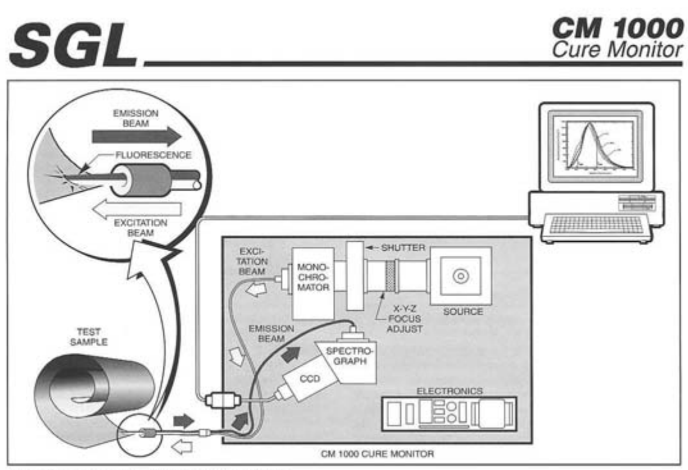
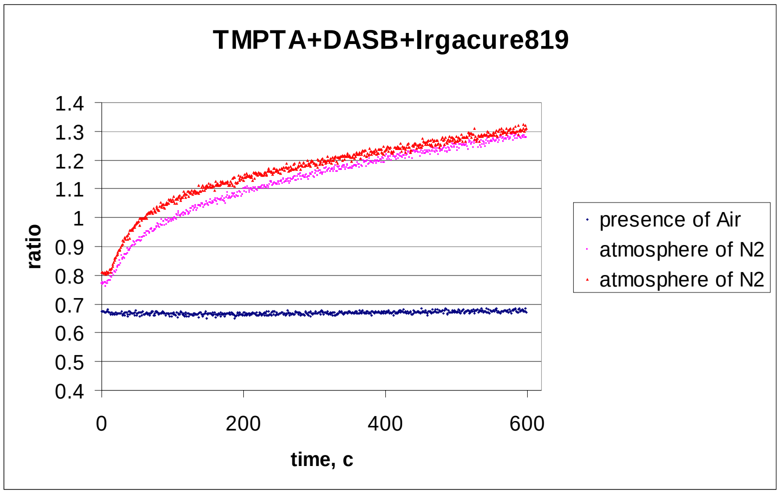


Fig. 1 Typical application of the CM 1000 Cure Monitor

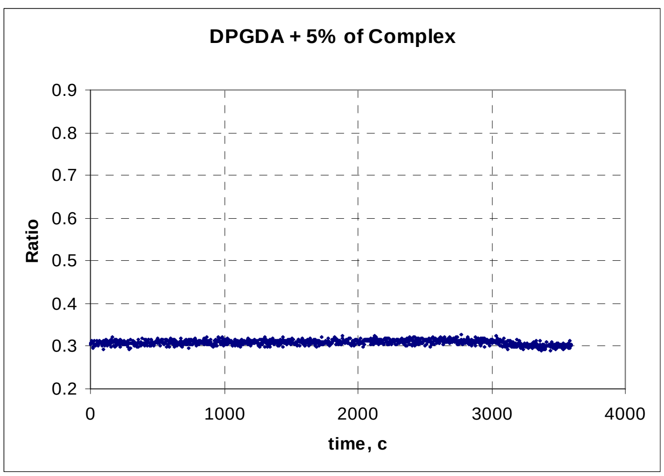
Commercial cure monitor - note exploded view of optical fiber excitation source and emission read out.

Use of CM-1000 for Monitoring the Real-Time Curing Profiles
1. Standard system

Excitation at 350 nm, ratio measured at 456/558 nm

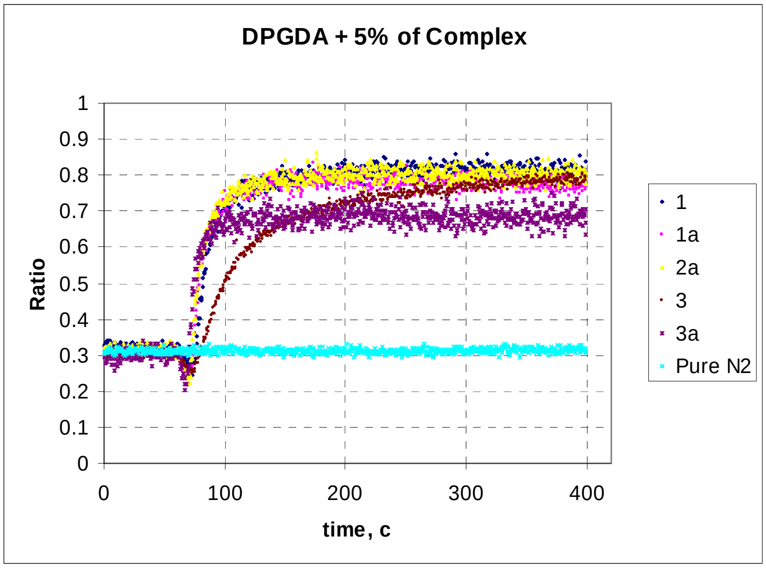


Stability of the System.
Flow of pure N_2, normal conditions.



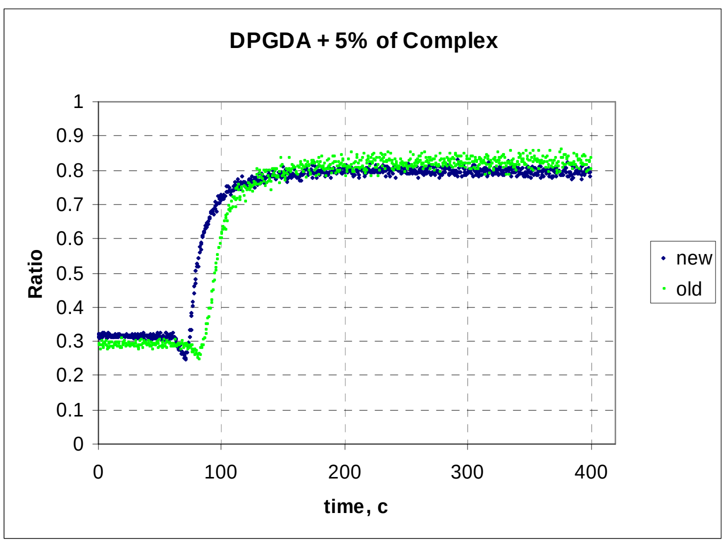
Result: No detectable changes were observed for at least 45 minutes

Reproducibility of the Real Time Curing Profiles



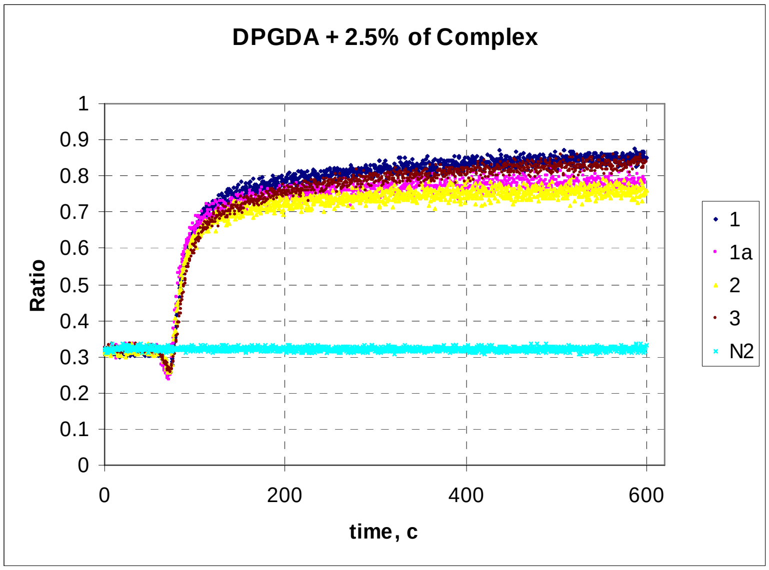
*Samples marked as "a" – the same as numbered, spectra taken 15 minutes later.
Experimental conditions: 33 ºC, humidity 95%.

Reproducibility of the Results – Shelf Stability of the Complex

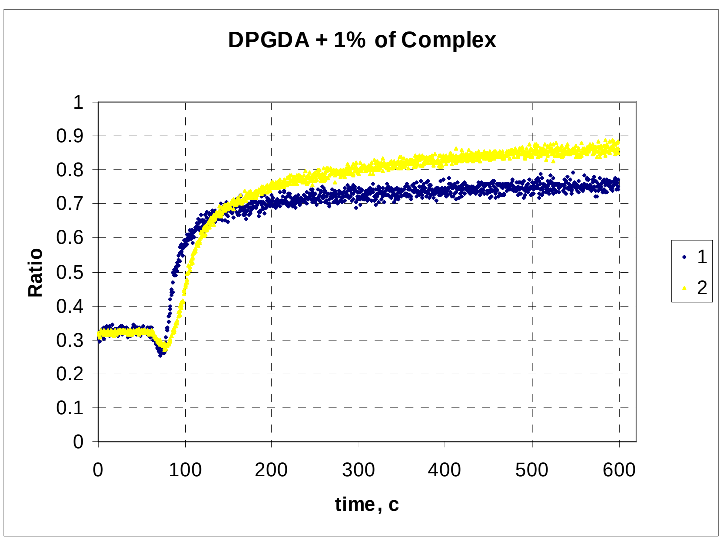


*Curve marked as "old" was obtained a week before "new".
The same sample of the Complex was used in both cases.

Reproducibility of the Real Time Curing Profiles



Reproducibility of the Real Time Curing Profiles



Work in progress/planned - *Remote cure*

- Mechanism/optimization/scope.
- Cure characteristics of approved corrosion resistant radiation curable paints - depth of cure, hardness, impact & corrosion resistance. In lab test panel experiments.
- Effect of other additives on cure characteristics.
- Establishing a basis set in field testing with currently approved paints (collaborative with Art Webb, ONR- trip to Key West in mid January essential).
- Field tests as indicated.

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Additional activities

- Redesigned cure monitor specifically applicable for remote cure work (collaboration with Ohio Laboratory for Kinetic Spectrometery/Wright Photosciences Laboratory).
- Evaluation of portable light sources as furnished by Navy SBIR contractors (collaborative with Spectra Group, Ltd.).
- Developing additional cure chemistries.

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Collaborators

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