Accelerated Aging Studies and the Prediction of the Archival Lifetime of Optical Disc Media

David E. Nikles* and John M. Wiest**
Center for Materials for Information Technology
University of Alabama
Tuscaloosa, AL 35487

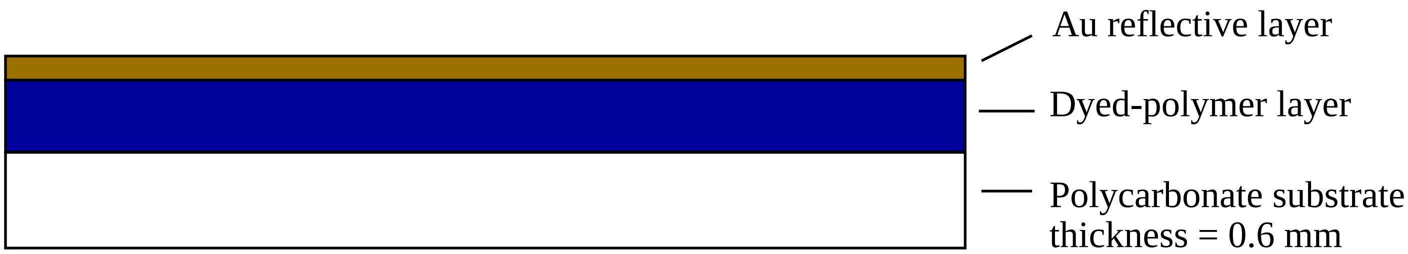
*Chemistry   **Chemical Engineering

Outline:

- Optical Recording
- Failure
- Some Data
- What is Accelerated Aging
- The Science of Accelerated Aging
- Sample Analysis Methods
- What is Needed

Optical Recording Primer

DVD-R



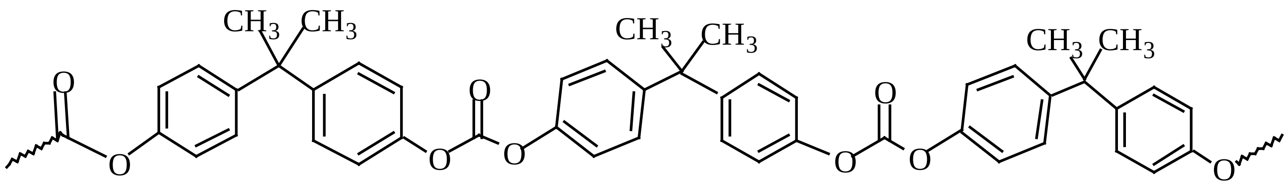
DVD-RW

Optical Disk Substrate Materials

Polycarbonate

Dominant substrate material

T_g = 150°C

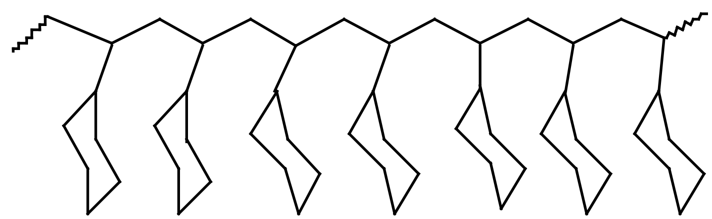


Polycyclohexylethylene

Dow Chemical

T_g = 146 to 150°C

Low birefringence



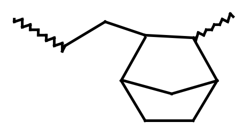
Topas®

Ticona

Random copolymer of ethylene and norbornene

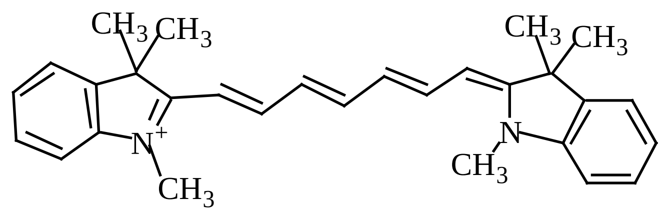
T_g = 70 to 225°C

Low birefringence



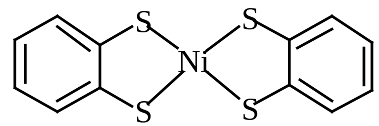
Dyes Used in CD-R Disks

Cyanine Dyes

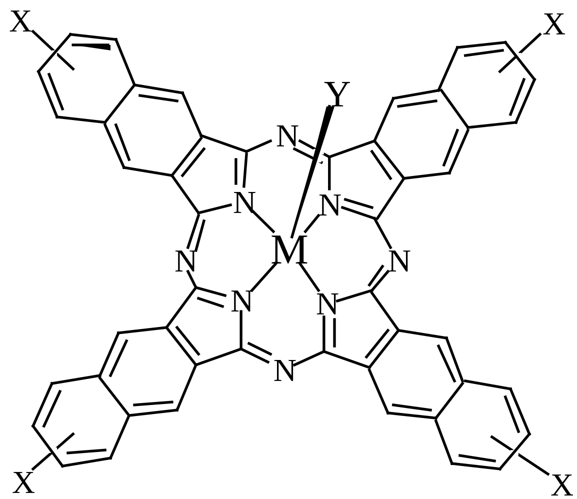


Nickel Bisdithiolate Complexes

stabilizer for cyanine dyes



Naphthalocyanines



Phase Change Alloys

Ge Te Sb Ag In Co Se Au Bi As

Failure

- All materials fail!
- Acceptable vs. Catastrophic Failure
- How will it happen?
- How long will it last?
- Do we care?

Physical Failure

- Polymer embrittlement
- Layer de-adhesion
- Birefringence from free volume consolidation
- others….

Chemical Failure

DVD-R

Expect the dye to be the weak link

Photochemical degradation

Reaction with moisture and oxygen (slow — reaction kinetics limited)

Reaction with ozone (fast — mass transfer limited)

DVD-RW

Corrosion of the phase change alloy

Requires diffusion of oxygen and water through the polycarbonate, through pinholes in the dielectric layers

Probably Mass transfer limited

Accelerating Aging Studies

Expose disks to high temperature and high humidity conditions

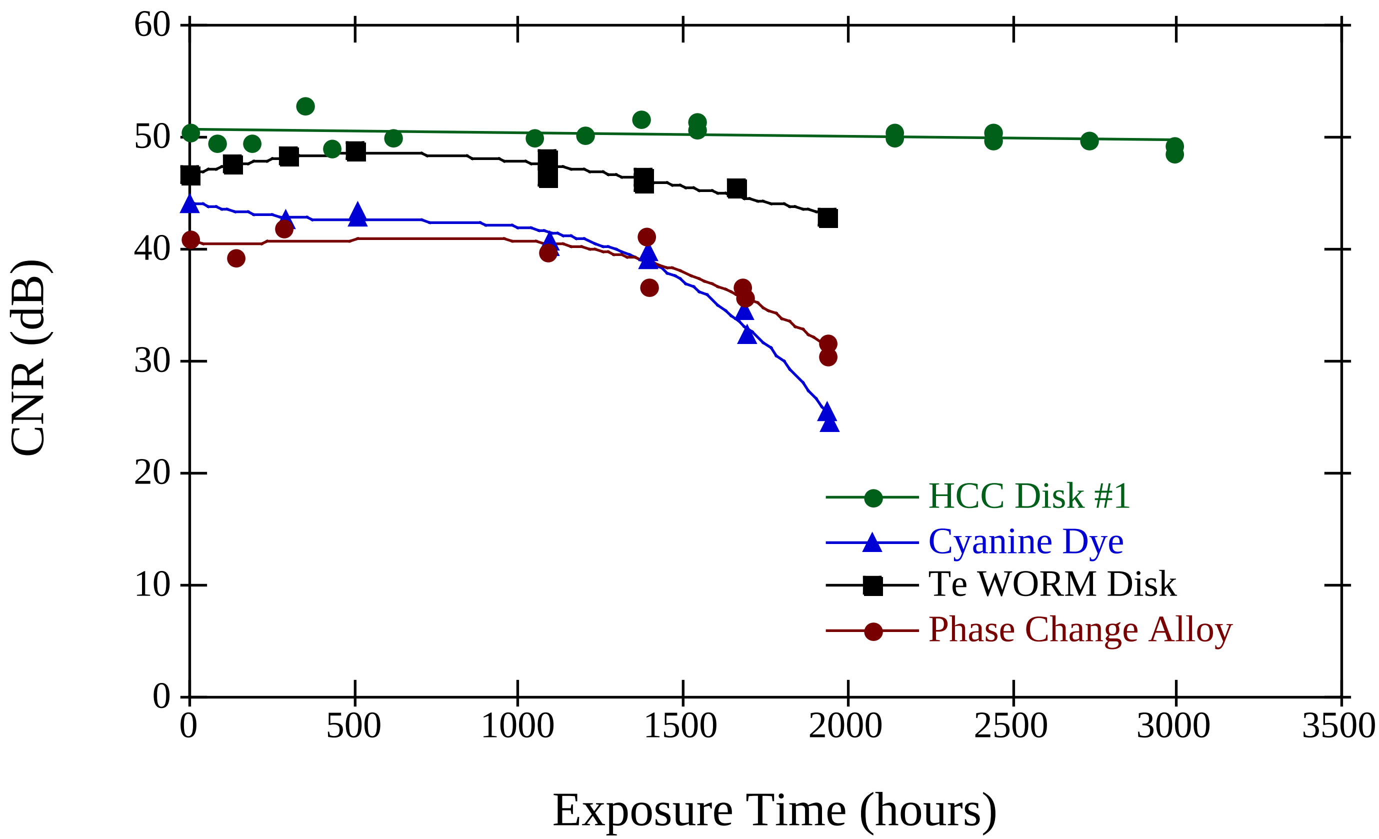
- 65°C and 80% relative humidity
- 80°C and 80% relative humidity
- 90°C and 90% relative humidity

Measure the carrier to noise ratio (CNR)

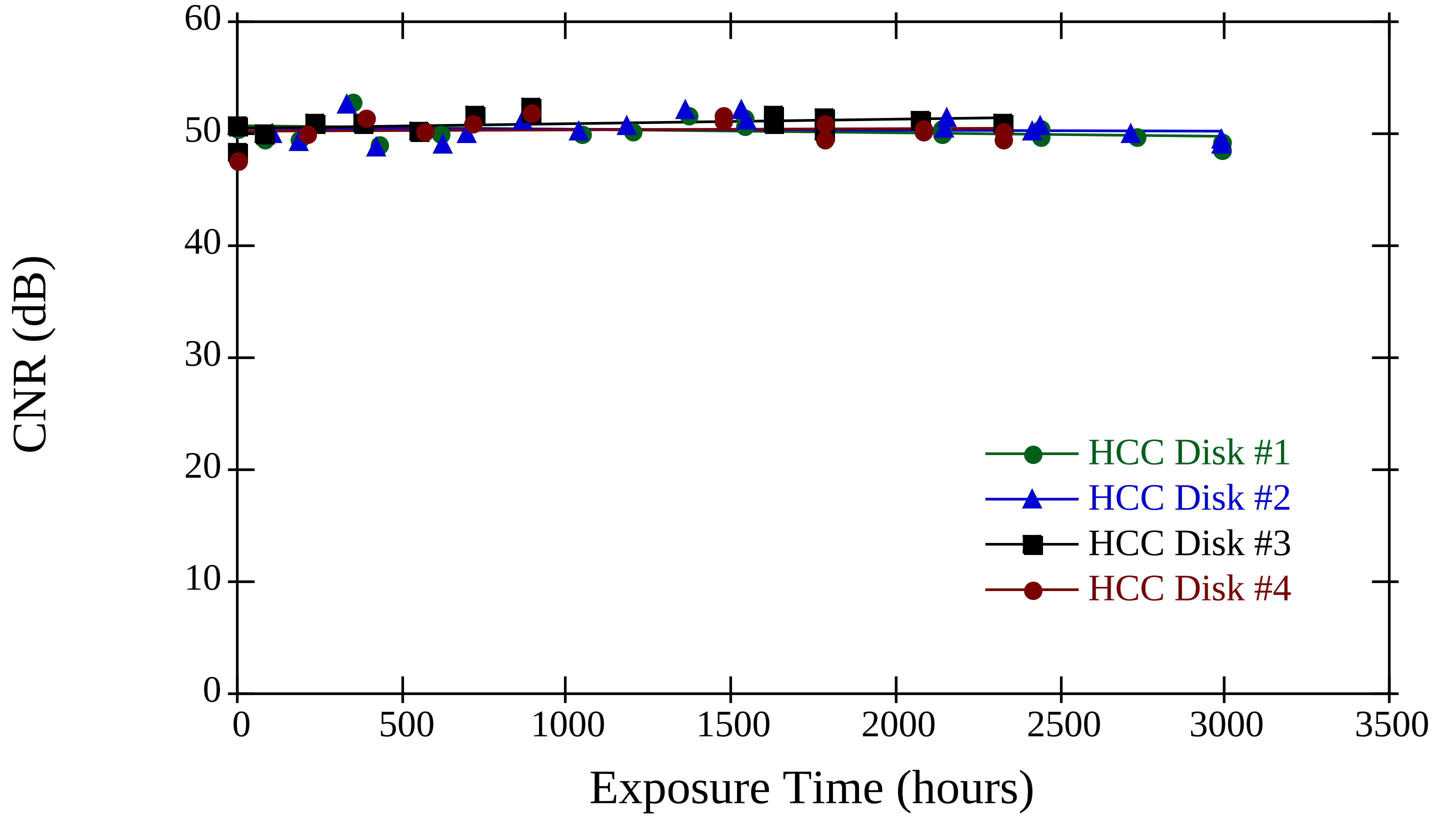
- 830 nm laser diode
- Record at 2.5 MHz carrier frequency
- Media velocity 5.65 m/s
- Read power 0.5 mW
- CNR in a 30 kHz bandwidth

D. E. Nikles, et al. Proc. SPIE-Int. Soc. Opt. Eng. **1078**, 43-50 (1989).
D. E. Nikles, et al. Proc. SPIE-Int. Soc. Opt. Eng. **1248**, 65-73 (1990).

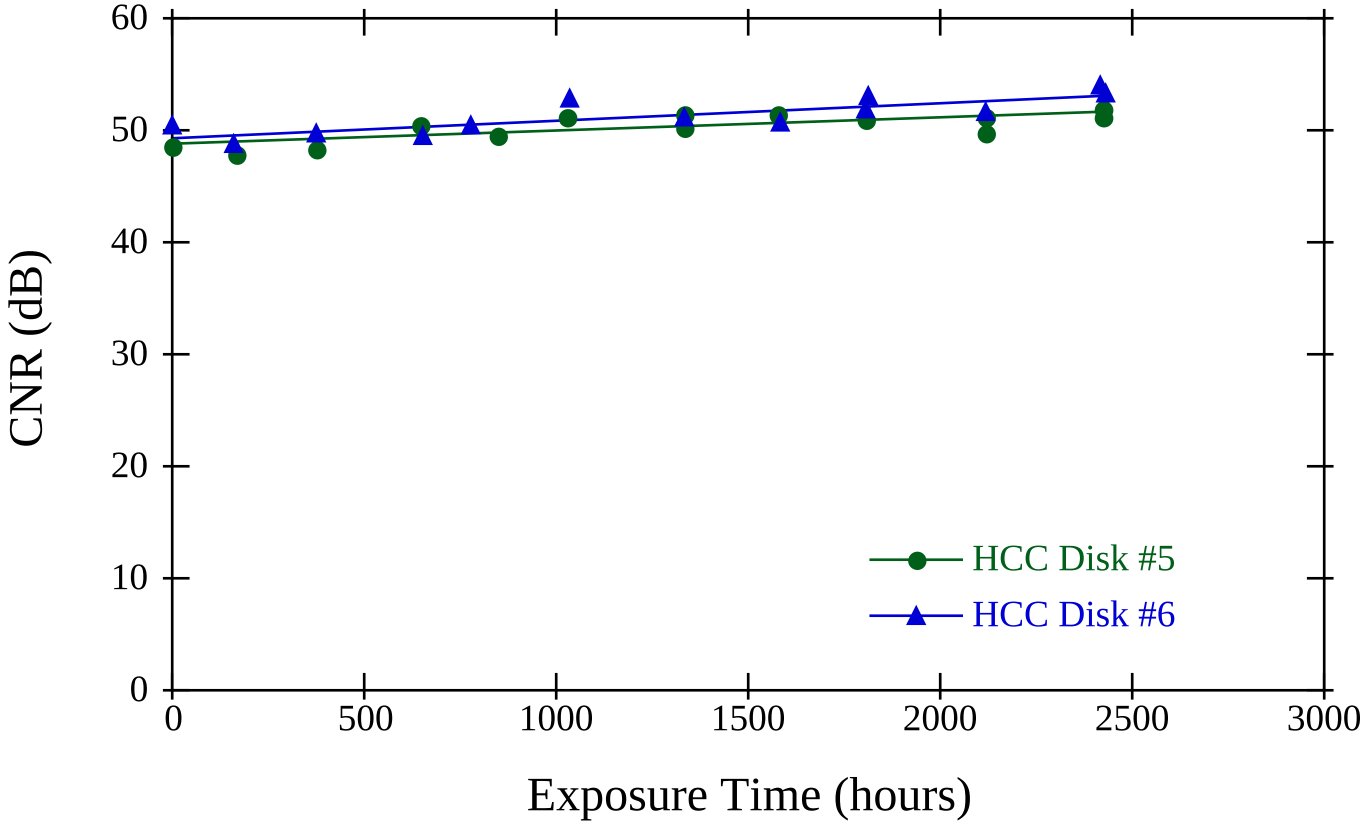
Accelerated Aging Studies at 80°C and 80% Relative Humidity



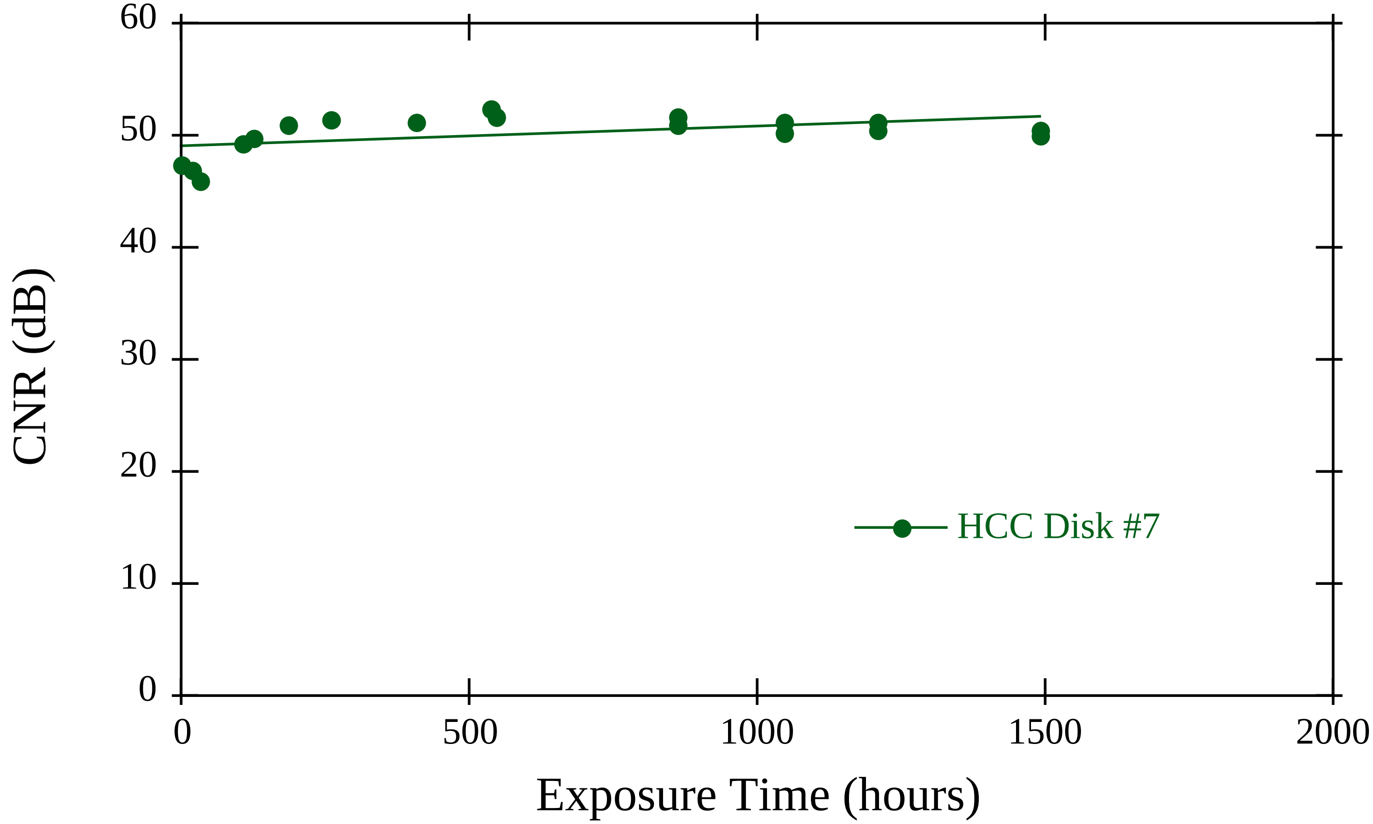
Disks Exposed to 80°C and 80% Relative Humidity

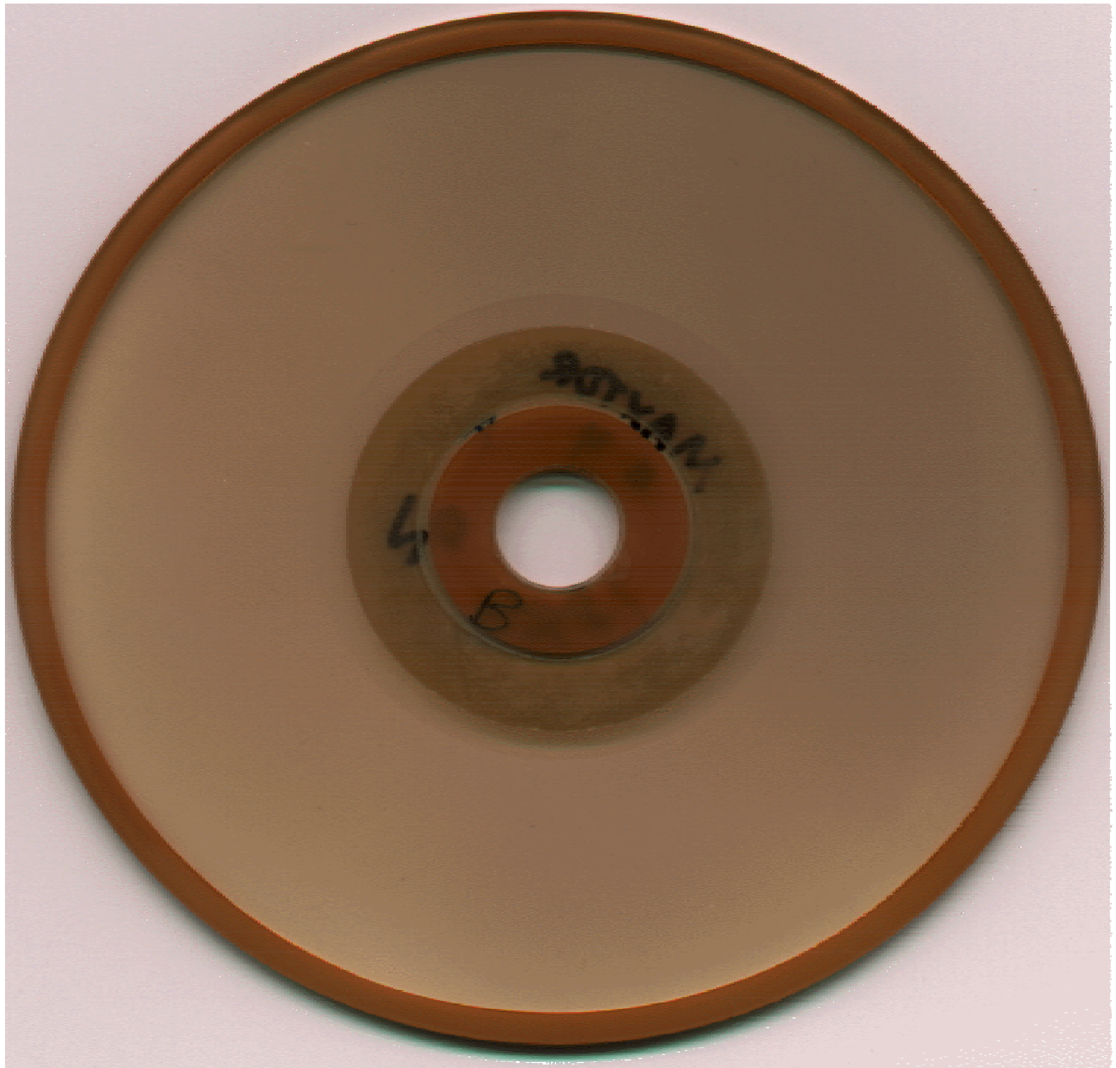


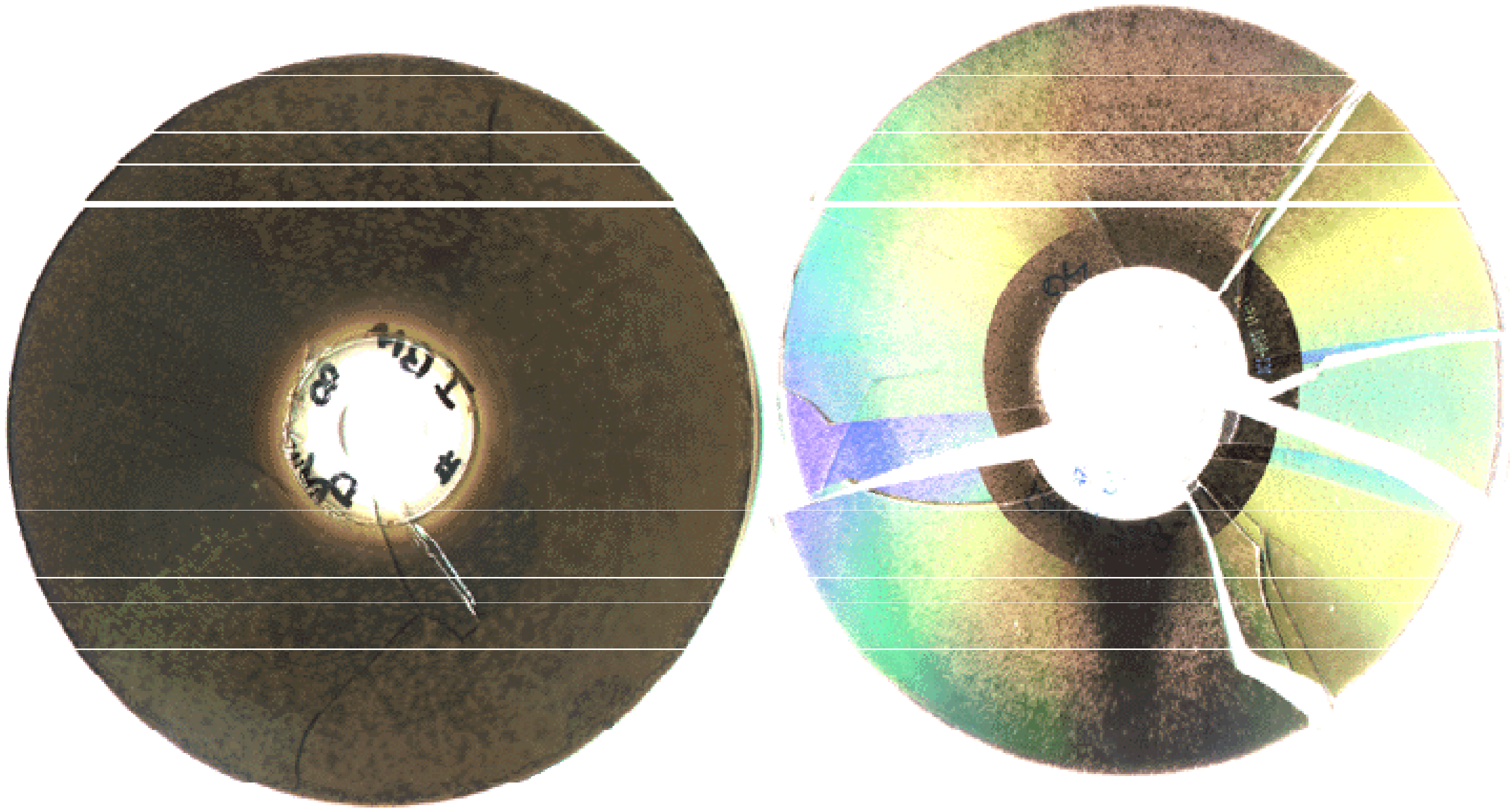
Disks Exposed to 65°C and 80% Relative Humidity



Disks Exposed to 90°C and 80% Relative Humidity







THE UNIVERSITY OF ALABAMA

Center for Materials for Information Technology

A NSF Materials Research Science and Engineering Center

Accelerated Aging

Can we change the environmental conditions to which a material is exposed and increase the rate at which degradation and/or failure occurs?

For example, elevated exposure to light, heat, or chemical 'bad actors.'

Can we do it in such a way that the results

- make sense?
- are useful?
- are predictive?

Material Clocks

Effect of Temperature:

A Gedanken Experiment

Material Clocks

How do we quantify this?

$$dt^* = \frac{dt}{a_X[X(t)]}$$

$$a_X = \frac{\lambda(X)}{\lambda(X_o)}$$

$\lambda =$ relaxation time

$X = \{T, c, \boldsymbol{\tau}, RH, \ldots\}$

Problems with Material Clocks

- Uniform X dependence of relaxation modes
- Phase transitions
- Determining $\lambda(X)$
- Multiple X's

Reactive Mass Transfer:

Conservation Relations

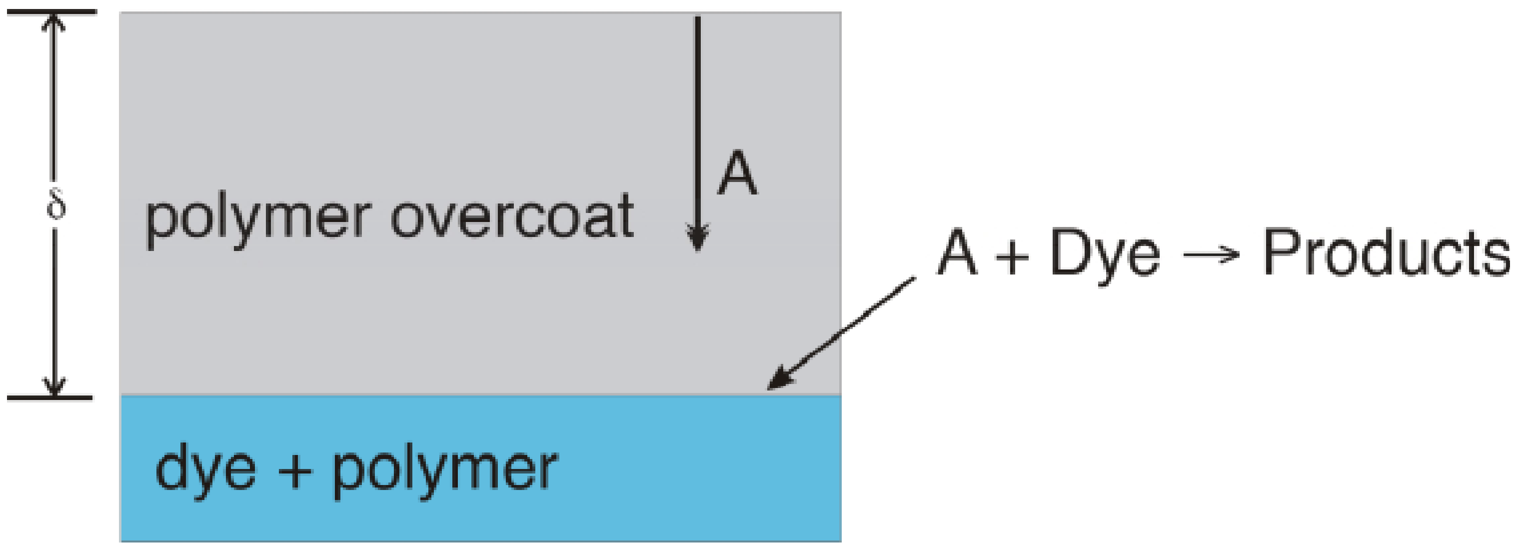
$$\frac{\partial c_i}{\partial t} = -\nabla \cdot J_i - R_i$$

R_i = rate of destruction of species i by reactions

J_i = mole flux of species i

$$J_i = -\sum_j \boldsymbol{D}_{ij} \nabla c_j$$

A Simple Example



Assumptions

- Steady State
- One Dimensional Diffusion
- Effective Binary System:
  - single penetrant with stationary substrate
- Fickian Diffusion
- Single Degradation Reaction
- Polymer Does Not Degrade
- Degradation Reaction Occurs at Interface

Kinetically Limited Case

Mass Transfer Rate >> Reaction Rate

Rate of Degradation = Rate of Reaction

Assume Arrhenius Temperature Dependence of Reaction Rate: $R_A \propto e^{-E_r/T}$

Then:

$$R(c,T) = R(c_o,T_o)\left\{\left(\frac{c}{c_o}\right)^n \exp\left[E_r\left(\frac{1}{T}-\frac{1}{T_o}\right)\right]\right\}$$

Mass Transfer Limited Case

Reaction Rate >> Mass Transfer Rate

Rate of Degradation = Rate of Penetrant Arrival at Interface

$$= \frac{-D_{AM}}{\delta} \ln(1 - x_{As})$$

Assume: $D_{AM} \propto e^{-E_d/T}$

Then:

$$R(T, x_{As}) = R(T_o, x_{Aso}) \left\{ \frac{\ln(1 - x_{As})}{\ln(1 - x_{Aso})} \exp\left[E_d \left(\frac{1}{T_o} - \frac{1}{T} \right) \right] \right\}$$

Reactive Mass Transfer:

Conservation Relations

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot J_i - R_i$$

R_i = rate of destruction of species i by reactions

J_i = mole flux of species i

$$J_i = -\sum_j \boldsymbol{D}_{ij} \nabla c_j$$

Assume first order kinetics: $R_A = -kc_A$

Then (as per Danckwerts):

$$c_A(r,t) = e^{kt} c_A^d(r,t) - k \int_0^t e^{kt'} c_A^d(r,t')\,dt'$$

Where $c_A^d(r,t)$ is the solution in the absence of reaction.

A material clock?

$$\text{Let}: \qquad ds = \frac{D_{AM}(T)}{D_{AM}(T_o)}\,dt$$

$$\text{Assume}: \qquad k(T) = k_o \exp\left[E_r \left(\frac{1}{T_o} - \frac{1}{T} \right) \right]$$

$$\text{Then}: \qquad c_A^d(r,t,T) = c_A^d(r,s,T_o)$$

A material clock!

But:

$$c_A(r,t,T) = e^{k_0\left\{\exp\left[E_r\left(\frac{1}{T_0}-\frac{1}{T}\right)\right]\right\}t} c_A^d(\mathbf{r},s,T_0)$$

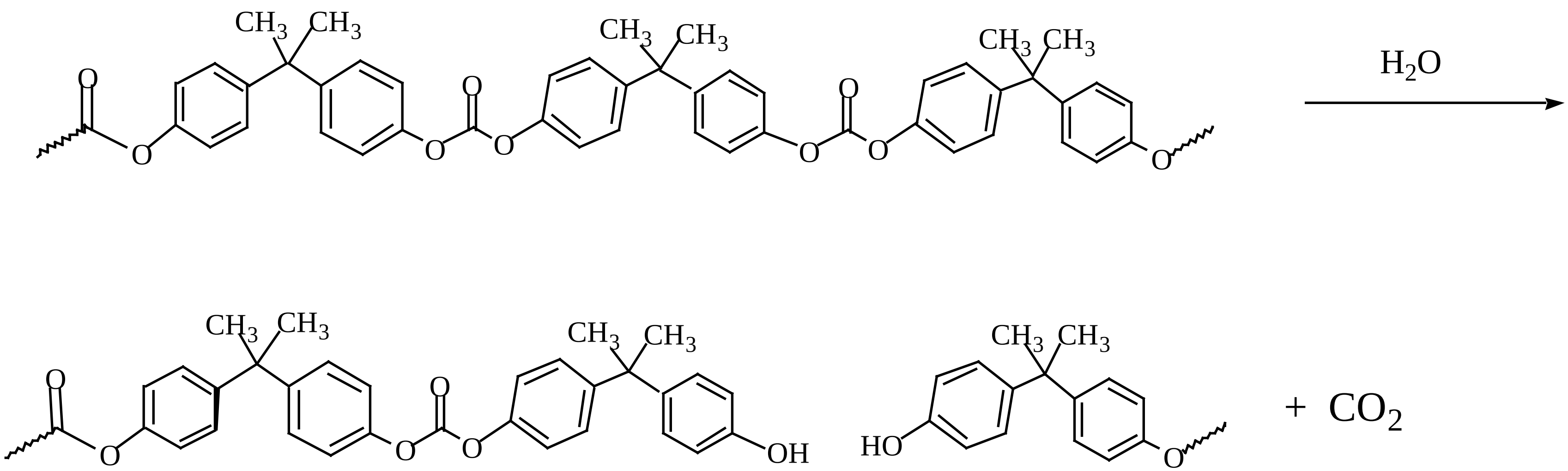
$$-k_0\left\{\exp\left[E_r\left(\frac{1}{T_0}-\frac{1}{T}\right)\right]\right\}\int_0^t \left(e^{k_0\left\{\exp\left[E_r\left(\frac{1}{T_0}-\frac{1}{T}\right)\right]\right\}t'} c_A^d(\mathbf{r},s',T_0)\right) dt'$$

Problems with Assumptions

- Multiple (many) species / Multiple (many) reactions
- Neither mass transfer nor diffusion limited
- Thermophysical properties vary with time
- Reaction products promote further degradation
- Mass transfer in polymers is not Fickian

and...

Polycarbonate Degradation



The ester linkages in polycarbonate are susceptible to hydrolysis

The activation energy for hydrolysis was 70 ± 4 kJ/mol

“Accelerated Aging Studies for Polycarbonate Optical Disk Substrates” D. E. Nikles and C. E. Forbes *Proc. SPIE* **1499**, 38-41, 1991.

Conclusions

The materials package is sufficiently complicated that a rational basis must be devised for accelerated aging.

Is it possible to find a suitable ‘material clock?’

Must identify the fundamental mechanisms of failure.

Require kinetic data (reaction and transport) for failure mechanisms.

There is a lot of work that could/should be done on this problem!