Looking at Plastics

An Introduction to Caring for Plastics

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Mary Coughlin
Assistant Professor
Director of Distance Education
Museum Studies Program
George Washington University
coughlin@gwu.edu

Types of Plastics

Natural Plastics

- Horn, hoof, tortoiseshell

Semi-synthetics

- Cellulose Nitrate, Cellulose Acetate

Synthetics

- PVC, Polyethylene

Plastics in many forms

- **Solid**: film or sheet, foam, block, rod, panel, textile
- **Liquid**: solution, emulsion, ashesive, dispersion (latex)
- **Composite**: sheets on foam core, laminates, fiber-reinforced plastics (fiberglass)

Types of Plastics

- <u>Thermoplastics</u>
  - Most plastics (~80%)
  - Soften when heated and harden again when cooled. Can be re-melted and re-shaped
  - Creep and deform under stress (more so at elevated temperature)
- <u>Thermosets</u>
  - cross-linked, permanently hard and rigid.
  - Can’t be re-melted or re-shaped

- <u>Elastomers</u>
  - Polymers that have the elastic properties of natural rubber
  - Resume original shape once is removed
  - Often made with PUR

Types of Plastics

Thermoplastics	Thermosets
Cellulose nitrate (CN)	Phenol formaldehyde (PF)
Cellulose acetate (CA)	Casein formaldehyde (CF)
Poly (vinyl chloride) (PVC)	Urea formaldehyde (UF)
Polyethylene (PE)	Melamine formaldehyde (MF)
Polystyrene (PS)	Polyurethane solids (PUR)
Polypropylene (PP)	Polyester
Polycarbonate (PC)	Hard rubber
Polyamides (PA)	

Polymers

- Long chain molecules formed from repeating molecular units (monomers)
- Polymer scientists make new plastics
  - Modify natural polymers
  - Create new polymers
- Fully synthetic plastics often named for their polymer. “Poly____”

Synthetics “Poly”

Poly (vinyl chloride) (PVC) 1927

Polyvinylidene chloride “Saran” 1933

Polyethylene 1934

Polymethyl Methacrylate (PMMA)

- “Plexiglas” “Lucite” “Perspex” 1934

Polyurethane 1937

Polystyrene 1937

Polypropylene 1954

Polycarbonate

- “Lexan” 1958

Polyurethane

- elastomer fibers spun into textiles “Spandex” or “Lycra” 1958

Plastic Developments

Most polymers invented on either side of WWII

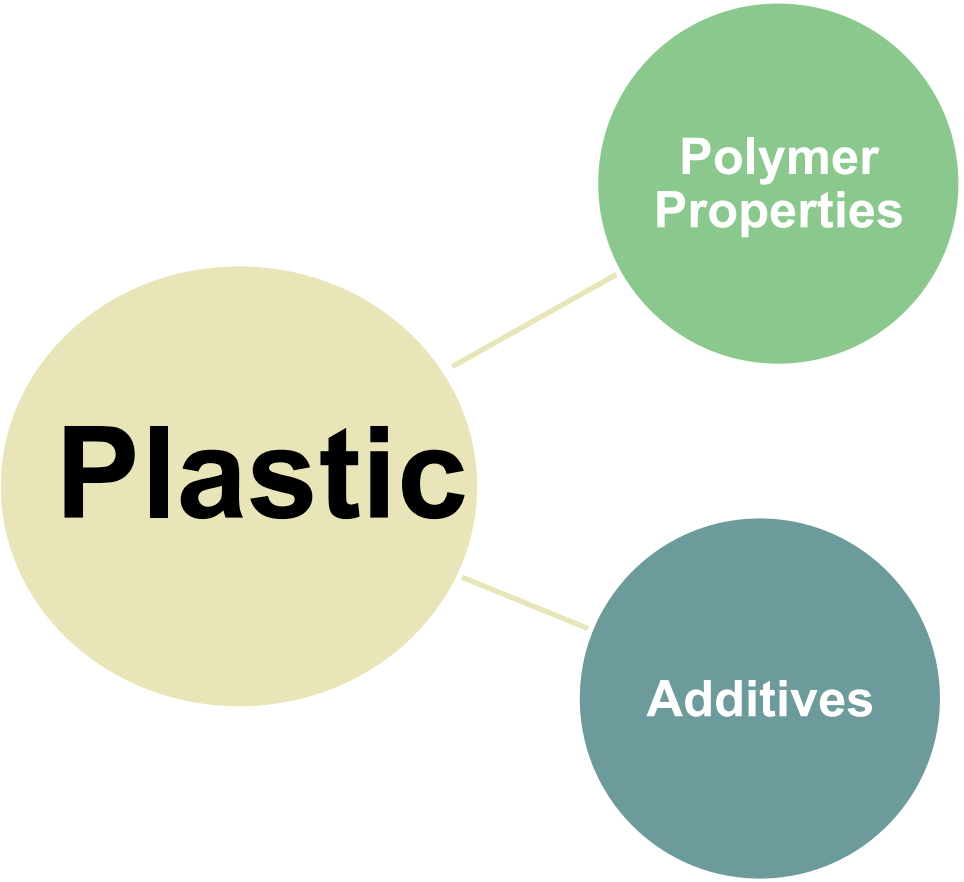
No significant new plastics introduced in decades!

- Expensive
- Time intensive
- Today, most polymer chemists modify existing base polymers

Tens of thousands of plastic formulations based on about 50 classes of plastics

1950-2017, 8.3 billion metric tons of plastic produced. About half made since 2004 (highest amount for packaging)

Formulating Plastics



- Molecular Weight
- Molecular Shape
- Degree of Polymerization

- Plasticizers
- UV blockers
- Antioxidants
- Colorants
- Heat stabilizers
- Fillers
- Processing aids
- Fire retardants

Plastic Additives

- Plasticizers:
  - Flexibility

Plastic Additives

Plasticizers

- Added to make more flexible
- Physical or chemical bond?

Take away for museums:

- Plasticizers may work their way out
- Loss can cause weeping; making rigid or brittle
- Unknown formulations affect aging even in same plastic family
- Past exposure matters

Plastic Additives

- Antioxidants and UV blockers
  - Added to counteract degradation from photo-oxidation

Faced window

Faced interior of room

Plastic Additives

Antioxidants and UV blockers

- Most plastics vulnerable to photo-oxidation
- Will become exhausted

Take away for museums:

- Oxygen accelerates aging
- Visible Light exposure should be limited
- Eliminate UV
- Unknown formulations affect aging even in same plastic family
- Past exposure matters

Plastic Additives

Heat Stabilizers

- Plastic may be vulnerable at high T
- Will become exhausted

Take away for museums:

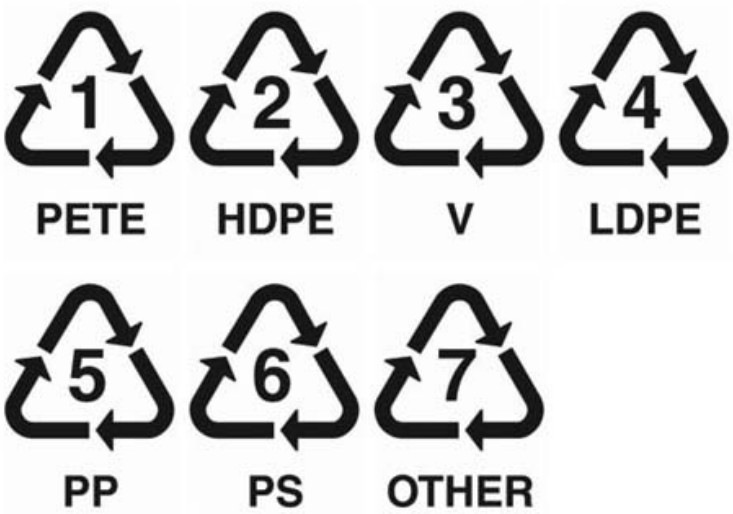
- Temperature matters!
- Lower T will slow chemical reactions
- Unknown formulations affect aging even in same plastic family
- Past exposure matters

Agents of Deterioration

- Physical Forces
- Thieves & Vandals
- Fire
- Pests
- Light
- RH
- Temp
- Water
- Pollutants
- Dissociation

Downcycled Plastics

- Recycled Plastics into new, lower grade plastics
  - Anti-aging additives used up and not replaced ($$$)
  - Heat in production can make even weaker



Bioplastics

- From renewable sources instead of petroleum
- **Biodegradable**
  - Intended to breakdown
- **Biobased**
  - PE, PET, PUR and PVOH can now be synthesized from plants
  - Polylactic acid (PLA)
    - Derived from corn, sugarcane, etc.
    - Used in 3-D printing
    - Will break down in high T and RH environments!

Commodity Plastics

98% of all plastics in daily life are “consumer plastics”

Poly(vinyl chloride) (PVC)	Polypropylene (PP)	Polystyrene (PS)
Polyethylene Terephthalate (PET)	Poly(methyl methacrylate) (PMMA)	Polyethylene (HDPE) (LDPE)

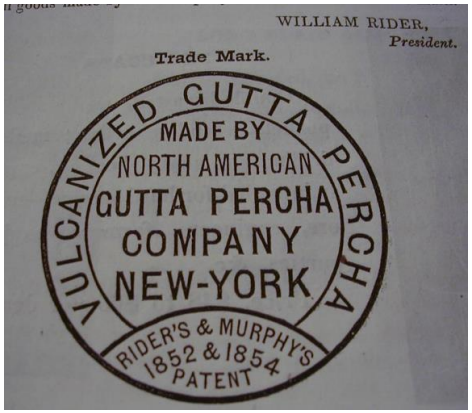
PE is most common plastic today

Commodity Plastics

- Polyethylene: milk jugs, grocery bags, Ziploc, Tupperware
- PVC: raincoats, squeeze toys, packing wraps, IV bags
- Polypropylene: monobloc chairs, yogurt tubs, caps
- Polystyrene: hangers, combs, Styrofoam
- PET: water bottles, fibers for clothes and carpets
- PMMA: “Acrylic”, “Plexiglas”, “Perspex”

How do you know?!?!

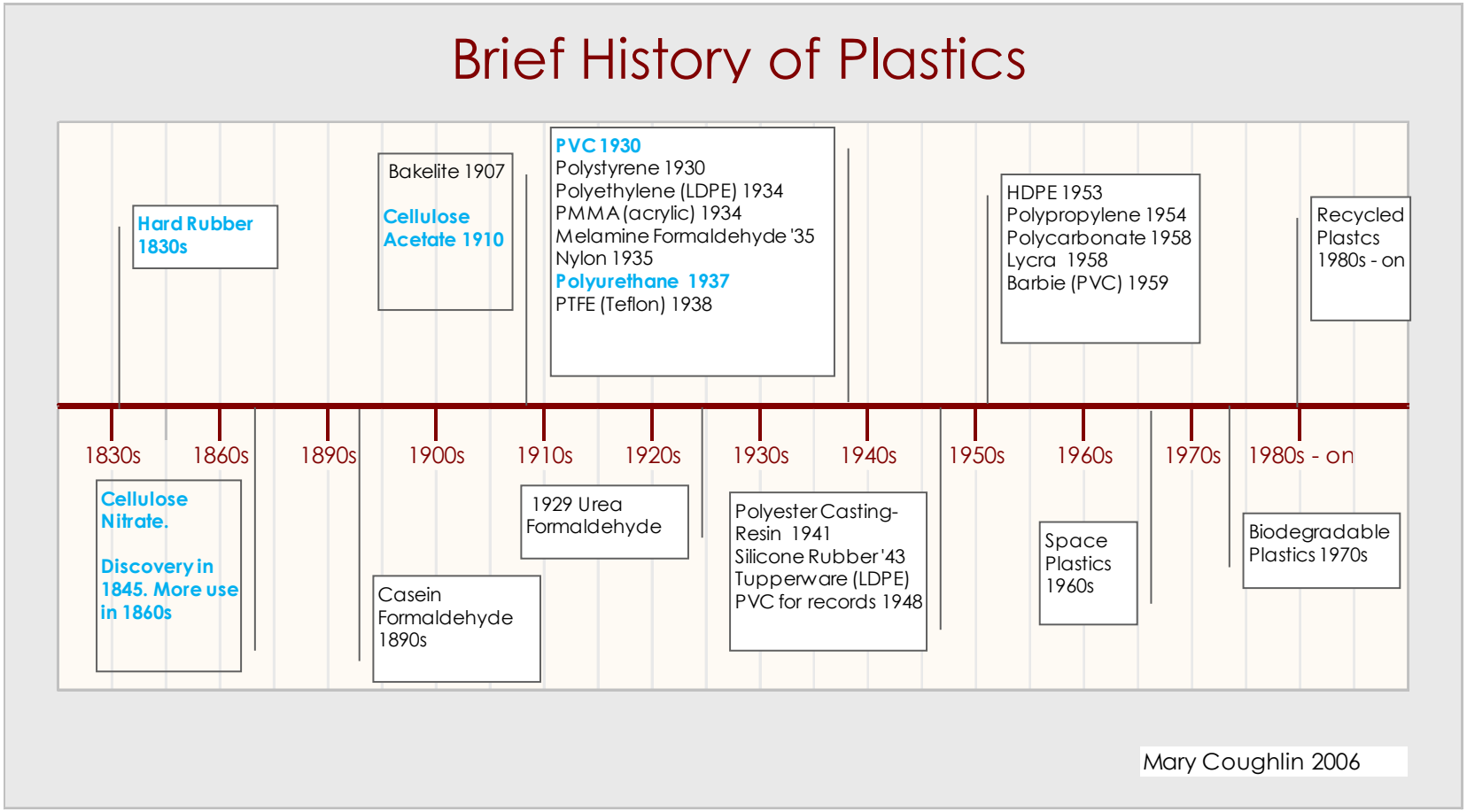
- Trademarks



- Tradenames
  http://bakelite_world_2001.tripod.com/itsbakeliteyouknow/id27.html

How do you know?!?!

Accession files - especially if give details about manufacture or use and a date, then narrow down options



Malignant Plastics

Hard Rubber

Cellulose Nitrate

Cellulose Acetate

PVC

Polyurethane

Urea formaldehyde often considered “aggressive to adjacent materials” because it can off-gas formic acid and can give off formaldehyde.

Hard Rubber

- <u>1830s / 1840s</u>
- “Vulcanite” or “Ebonite”
- Made from adding sulfur to rubber
- Can off-gas sulfuric acid
- Often turns brown or greenish as ages

Hard Rubber Deterioration

- Oxidation (reaction with oxygen)
- Up to 40% sulfur by weight
- Can off-gas sulfuric acid and be a risk to other materials
- Often turns brown or greenish as ages

Hard Rubber Conservation

- May benefit from oxygen free storage
- But if not an option, default to venting
- In general want RH 35% - 45%.

Cellulose Nitrate (CN)

- <u>1860s</u>
- Used as an explosive and as a plastic
- Translucent (if no colorants or fillers added)
- “Parkesine” (1861, in Britain) and “Celluloid” (1870, USA)
- “Ivroid” and “Xylenite” names for CN imitation ivory

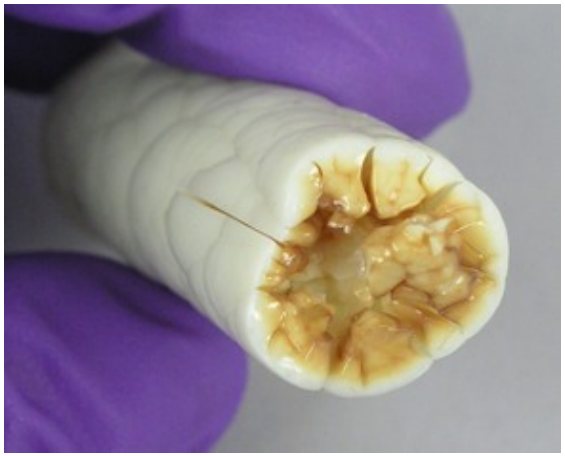
Cellulose Nitrate Deterioration

- Made by soaking cellulose pulp in a mixture of nitric acid and sulfuric acid.

- Deteriorating CN emits reactive nitrous oxides that can be converted to nitric acid by moisture
  - **Hydrolysis** starts at **50% RH**

- Nitric acid can form an oily film on the surface.
- Camphor plasticizer can sublime and leave small holes, water penetrates and forms nitric acid inside.

Cellulose Nitrate Deterioration



Cellulose Nitrate Deterioration

CN can off-gas acids and eventually crack as it deteriorates

Cellulose Nitrate Deterioration

Deteriorated Cellulose Nitrate Film in rusted containers

1st toothbrush with nylon bristles and CN handle

“Ivory” CN

- Zinc oxide pigment & filler
- Zinc can convert nitric acid to stable zinc nitrates
- Opaque colors may block light
- Usually ages well

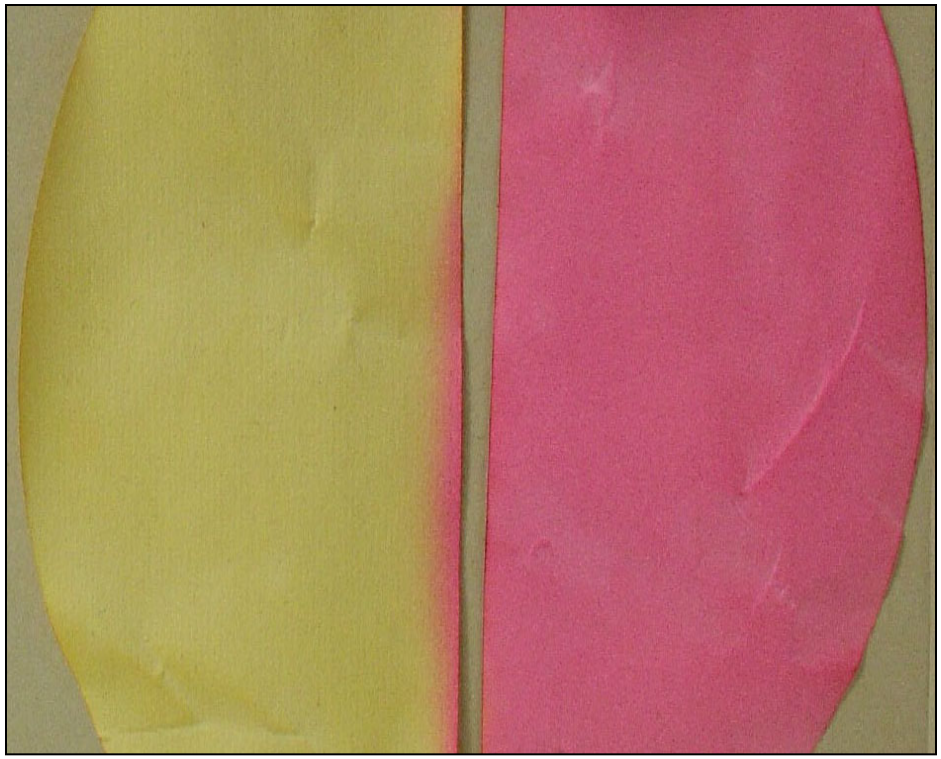
Cresol Purple or Red

- Potential accession
- Isolate and not accession off-gassing cellulose nitrate

Cresol Purple or Red

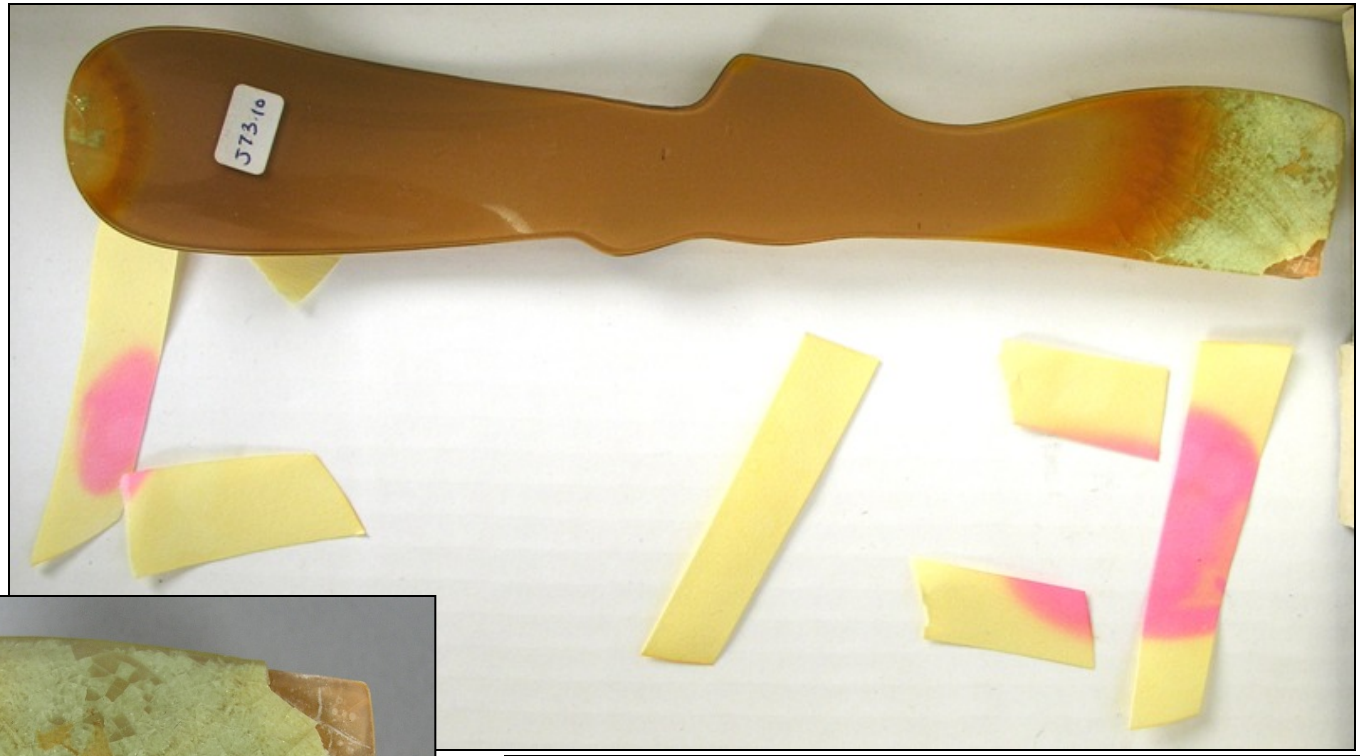
- Cresol Red or Purple are sensitive to vapor from <u>deteriorating Cellulose Nitrate</u>

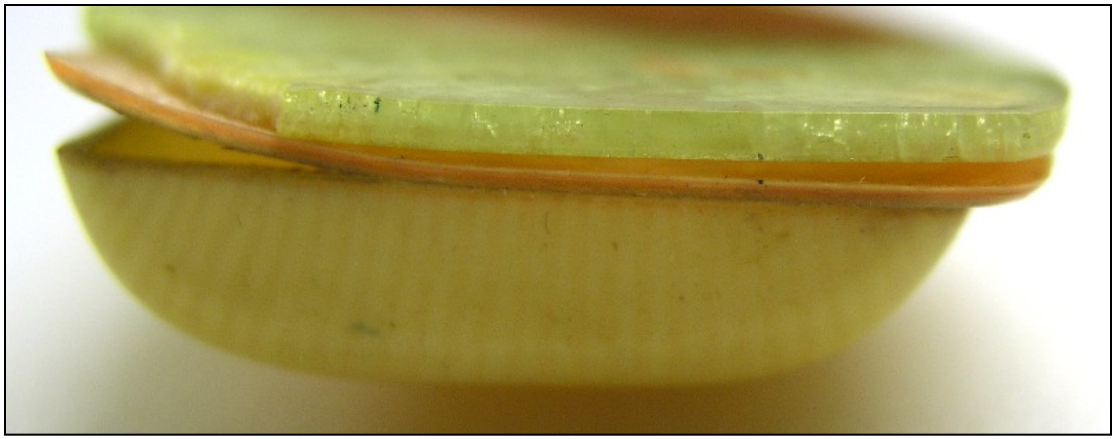
- Change from yellow to pinkish color



After 1 day

After 1 week





Ivory top with 2 layers of other CN

Cellulose Nitrate Deterioration Detection: Cresol Purple Strips

Initial placement

Reaction after 1 day

Reaction after 1 week

Cellulose Nitrate Conservation

Monitor for off-gassing

In general want RH 35% - 45%. Keep stable

- above 50% CN can form nitric acid from hydrolysis
- below 25% can craze plastics

Cool or cold storage

Ventilation

Storage in archival corrugated board (blueboard)

Cellulose Acetate (CA)

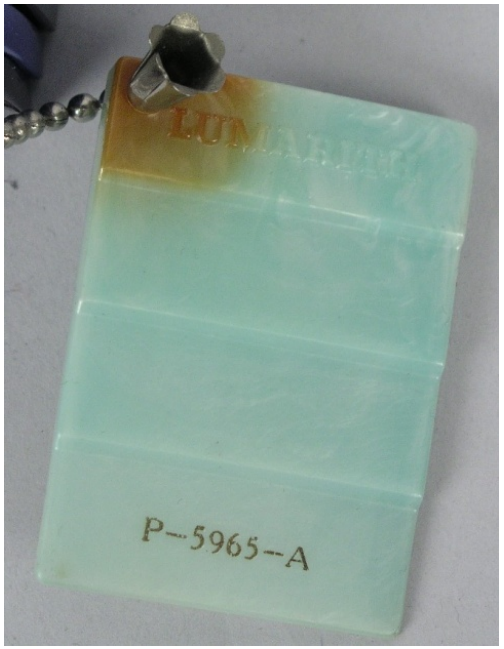
- 1910
- “Lumarith” “Tenite” “Safety Film”
- Two common grades:
  - Cellulose Triacetate (CTA)
  - Cellulose Diacetate (CDA)
- Used in same ways as CN but not as versatile
- Use slowed in 1960s but still used today
  - Now being looked at as a biodegradable plastic

Cellulose Acetate Deterioration

- Made from cellulose pulp, acetic acid, sulfuric acid
- Acetic acid (Vinegar Smell) and sulfuric acid compounds given off
- **Hydrolysis** at **50% RH**
- Loose Plasticizers
  - Sticky, acidic surfaces
  - Warping
  - Breakage

Cellulose Acetate Deterioration

- Same environment and manufacturer
- Why some deteriorated?
- Triphenyl phosphate additive
  - Reduces flammability
  - Health hazard, environmental risk
  - Associated with extreme degradation
- *Studies in Conservation* article



Deteriorated Cellulose Acetate Film with Channeling and Buckling

Cellulose Acetate Deterioration

Potato slices in CA , 1940s

Mosquitoes in PMMA, 1940s

Cellulose Acetate Deterioration

- Degradation rates double if acetic acid is not removed and pH reaches 4.6
- In past, adsorbents like zeolites used to counteract acid build-up
- Archival corrugated boxes (blueboard) better at slowing degradation
- Blueboard is acid and lignin free, typically buffered with 3% calcium carbonate and maintains a pH of 7.5-9.5 (CAMEO website)

Cellulose Acetate Deterioration

- Stacked storage trays
  - Blue board
  - Ethafoam spacers
- Ventilation
- May adosrb acidic off-gassing
- Lessen handling

Cellulose Acetate Conservation

Plasticizers vulnerable to high RH and will come out and can’t go back in

- RH higher than 50% can cause acetic acid to come out
- RH 35% - 45%

Degradation rate increases as T rises. Cool/cold storage

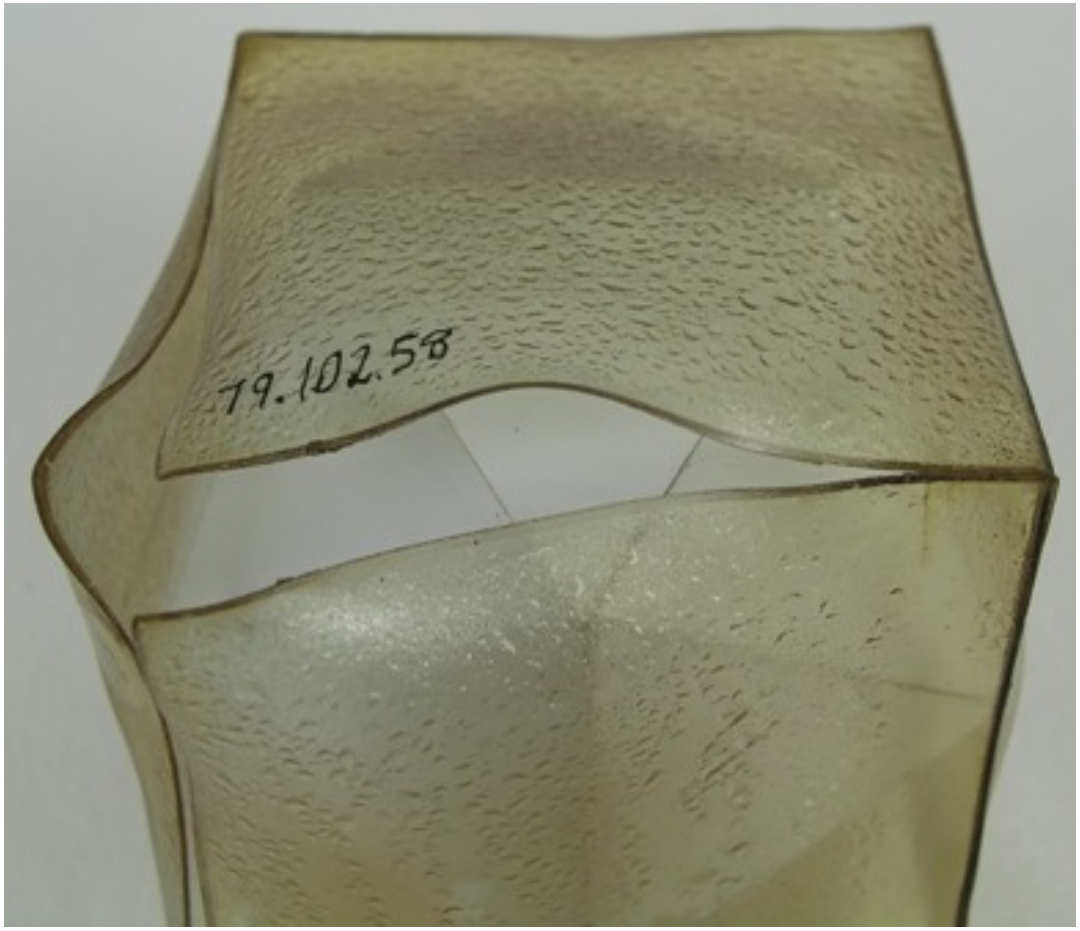
Ventilation

Monitor for off-gassing

Storage in archival corrugated board (blueboard)

Cellulose Nitrate & Cellulose Acetate

Cellulose Nitrate & Cellulose Acetate



math models before deaccessioning

Cellulose Nitrate & Cellulose Acetate

- CA sheet
- Weeping material crystallized at lower RH

Section of math model after deaccessioning

Poly(vinyl chloride) PVC

- Invented 1927 “Vinyl”
- Ethylene from natural gas is reacted with chlorine to produce vinyl chloride monomer. This is then reacted to form the polymer, poly(vinyl chloride)
- One of the top selling plastics in the world
  - Cheap production since less oil and natural gas needed
- For long time assumed to be chemically stable and safe
  - Thought archival until 1970s (bubble wrap)
  - Workers started getting sick from vinyl chloride gas
  - Additives started leaching out
    - “Humans are just a little plastic now.” Washington Post, 1972

PVC

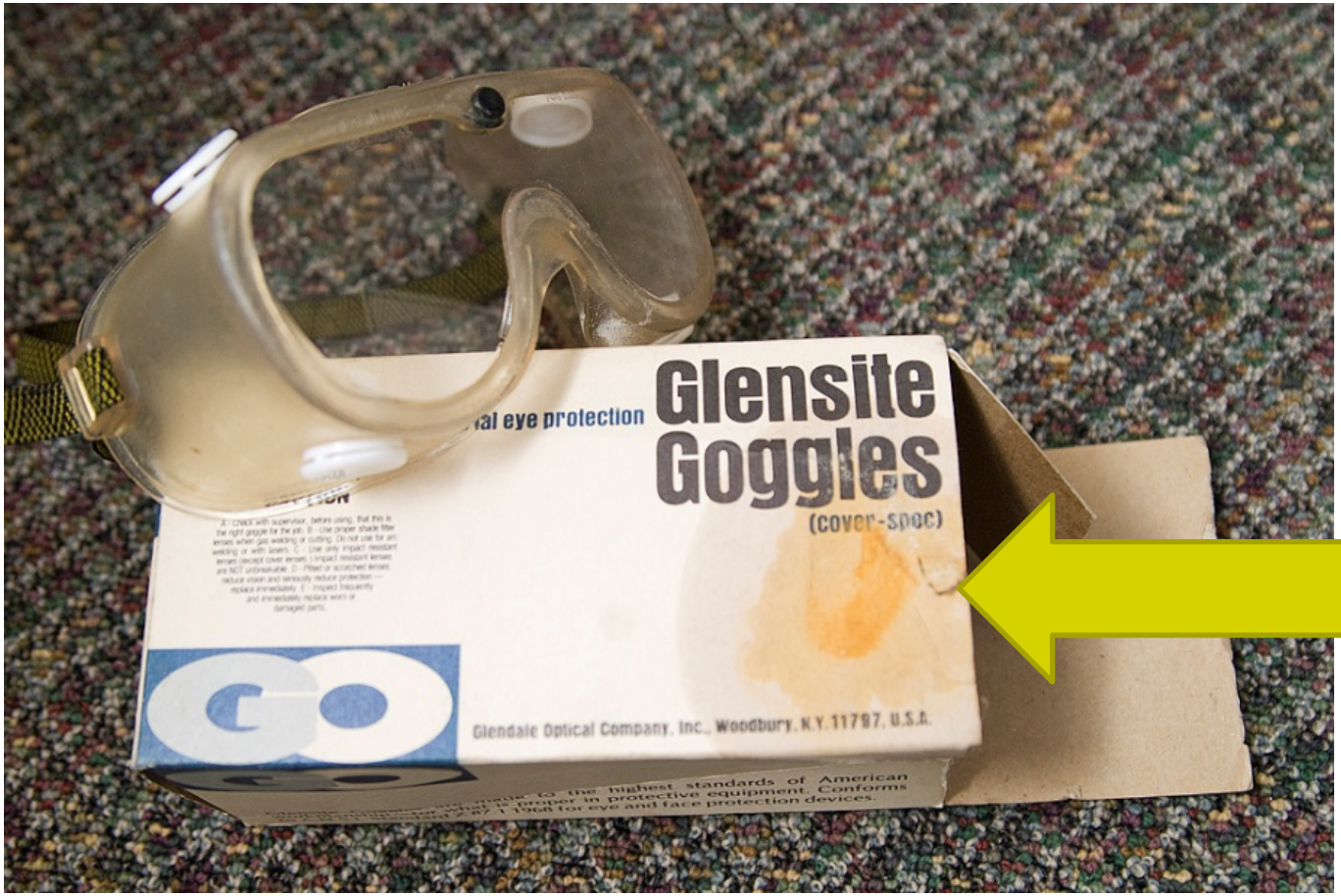
- Plasticizer
  - Can have 30% - 40% of the weight
  - Not strongly bonded
  - <u>If no plasticizers will last longer but most PVC is plasticized</u>
  - Some are toxic
- Phthalates
  - In many soft, pliable PVC
  - Clothing, rain coats, shower curtains, furniture, toys, wallpaper, cosmetics, adhesives, inks, varnishes, paints, time-release coating for medicine and supplements

PVC Deterioration

- Temperature or light induces degradation
  - May release hydrochloric acid – corrodes metal, etc.
  - Polymer cross-links
- Plasticizers migrate out with changes in T, stress, high RH
  - Can evaporate or sit on the surface
  - Blooms, weeps, shrinks, cracks, rigid
- Becomes less translucent with age and often discolors

PVC Deterioration

PVC Deterioration



Identified as PVC with FTIR , XRF, and Beilstein Test

Weeping material from PVC goggles soaked through the box

PVC Deterioration

Major categories of use and expected lifetimes of PVC products

Category	Example	Average lifetime (years)
Building	Window frames	10-15
Packaging	Film and sheet	1
Furniture	Fake leather upholstery	17
Household appliances	Tubing	11
Electric and electronic	Cable insulation	21
Automotive	Steering wheel cover	12
Others	Blood bags	2-10

*Shashoua, *Conservation of Plastics*, page 10

PVC Conservation

- If possible, remove PVC from general storage
- Heat and light are primary causes of deterioration
- In general want RH 35% - 45%.
- Degradation may be slowed by enclosure in a non-adsorbent container or put in a freezer (freezing less effective if PVC is severely degraded)
- Never use adsorbent (like zeolite) with PVC since will suck out the plasticizer

Polyurethane

- Invented 1937 by Bayer in Germany
- Commercially available 1950s

- Can be made in various forms:
  - Elastomer (soft and hard rubbers)
  - Foam (flexible and rigid)
  - Coatings
  - Adhesives
  - Fibers

Polyurethane

Fibers

- Variety of stretchy fabrics
- Never 100% PU
  - PU fibers blended with natural and manmade fibers
- Spandex – Lycra (1958)
- “Two-way Tricot”
  - PU fiber knitted with nylon or polyester filament yarn
  - Leotards
  - Swimsuits

Polyurethane

Thermoplastic PU

- Used where need strength and moisture resistance
  - Coating
    - Coat fabric to imitate leather
  - Adhesives
  - Sealants
  - Paints
  - Elastomers

Polyurethane

Thermoset PU

- Flexible Foams
  - Cushions
  - Mattress
  - Car interiors
  - Packaging
- Rigid Foams
  - Insulation
- 75% of PU is made into foams

PU Foams

1. **Polyurethane <u>ether</u>**
   - Photo-oxidation *(degradation catalyzed by oxygen or ozone and light)*
   - Starts to powder at surface
   - Yellows, discolors
   - Sunblock treatment option
2. **Polyurethane <u>ester</u>**
   - Hydrolysis (*degradation catalyzed by high RH*)
   - Reaction produces acids – autocatalytic and fast!
   - Degrade quicker than PU ether foams
   - No conservation treatment, yet

PU Foams

Ester or Ether?

- Near infrared spectroscopy analysis (no sample)
- FTIR analysis (small sample)
- 1 mm sample in 10% KOH solution
  - PU Ester dissolves
  - PU Ether does not dissolve

PU Foams

If not sure of type, assume:

- Large pores = more surface area so vulnerable
- Light sensitive but degrades in the dark
- VOCs can come out – particularly at high T
- Oxidation results in severe degradation

PU Foams

- Coated or painted foams may age better
  - Protection from light and oxygen

- Non-coated foam “useful lifetime” is 20-25 years
  - Crumbles
  - Depends on thickness

Polyurethane Deterioration

- Rub a clean glass slide over service, may see smear on glass
- Brittle as ages
- Can off-gas VOCs
- Discolors
- Yellows
- Doesn’t bounce back
- Looses its shape

Polyurethane Deterioration

Polyurethane Conservation

Anoxic environment can be beneficial as long as monitored to ensure that degradation products are not building up.

"Sunblock" treatment

- **PU <u>ether</u> foams ONLY!**
- Consolidate degraded foam
- Protects from light like applying sunblock

Polyurethane Conservation

If not in anoxic storage, then ventilate.

Don’t allow polyurethane to touch other materials or itself since it may stick – can use silicone or Teflon coated interleaves (can stick too!)

Keep in dark, if possible

Eliminate UV

If PU ester foam, may want low RH storage

- Hydrolysis at high RH

Plastic Textiles

Fibers may be plastic (PU) or may have plastic coating (PVC or PU)

Rapid development of man-made fibers start in early to mid 20th century

Plastic Textiles

- finer fibers have higher surface-area-to-volume ratios making them more chemically reactive to light and photo-oxidation than thicker ones

Plastic Textiles

- Unlike 3-D plastics objects, film, or coating of the same composition, aged plastic fibers appear more physically stable.
  - Chemical and mechanical properties from production
  - Extrusion process orients fibers:
    - Outer (skin) more oriented, more crystalline
    - Core is amorphous
  - Thickness, light, tension, past exposure all impact aging

Malignant Plastic Deterioration

Cellulose Nitrate	Crazes, tears and cracks. Becomes brittle. May be covered in a white layer. Releases acidic and/ or camphor odor. Droplets can appear on surface (misting, fogging). If in contact with metal, metal will corrode.
Cellulose Acetate	Tears, cracks, becomes distorted. Droplets can appear on surface. Releases acidic odor (vinegar smell). If in contact with metal, metal will corrode.
PVC	Weeps, often tacky. Can deform, harden and discolor.
Polyurethane	Foam discolors, crumbles
Hard Rubber	Turns brownish. If in contact with metal, metal will corrode

Good Plastic Gone Bad?

Good Plastic Gone Bad? Bakelite

- 1907
  - Wood flour, paper, asbestos and other fillers added to phenol formaldehyde resin
  - Good heat insulator
    - Radios, electrical plugs, telephone, hairdryers
  - Stable over time (some may form a bloom)
  - UV degrades

Bakelite Case Study

Evolving Studies

Some now think that Polyethylene and Polypropylene should be avoided

- Don’t emit acids
- Some don’t age well
- <u>Don’t store plastics in polyethylene bags</u>
  - Permeable and adsorbent
  - Can get migration of plasticizers into bags
  - If have to bag, Mylar bags are better

Evolving Studies

Original Tupperware (PE) in storage. Stickiness resulted in use of Plexiglas barriers.

Evolving Studies

PE will first yellow as oxidation causes formation of carbonyl groups and other chromophores, then disintegrates and smells 'sweaty‘ - antioxidant additives delay process but get exhausted over time.

All Plastics

Keep in a stable environment

- Monitor RH
- Lower T (cold storage or freezing, if possible)
- Keep in dark
- Look at artifacts around plastics

Think of plastics as PERMEABLE

- Some better barriers to water or oxygen
  - *PE keeps water out but lets oxygen in*
  - *Mylar is a good gas barrier*

Avoid stress

- Think how used or how made
- Labeling can cause stress

If object is distorted, often means off-gassing

All Plastics

Ventilate

- Prevent build-up of acidic gasses
- May not be best for PVC

Acid-free or buffered storage trays

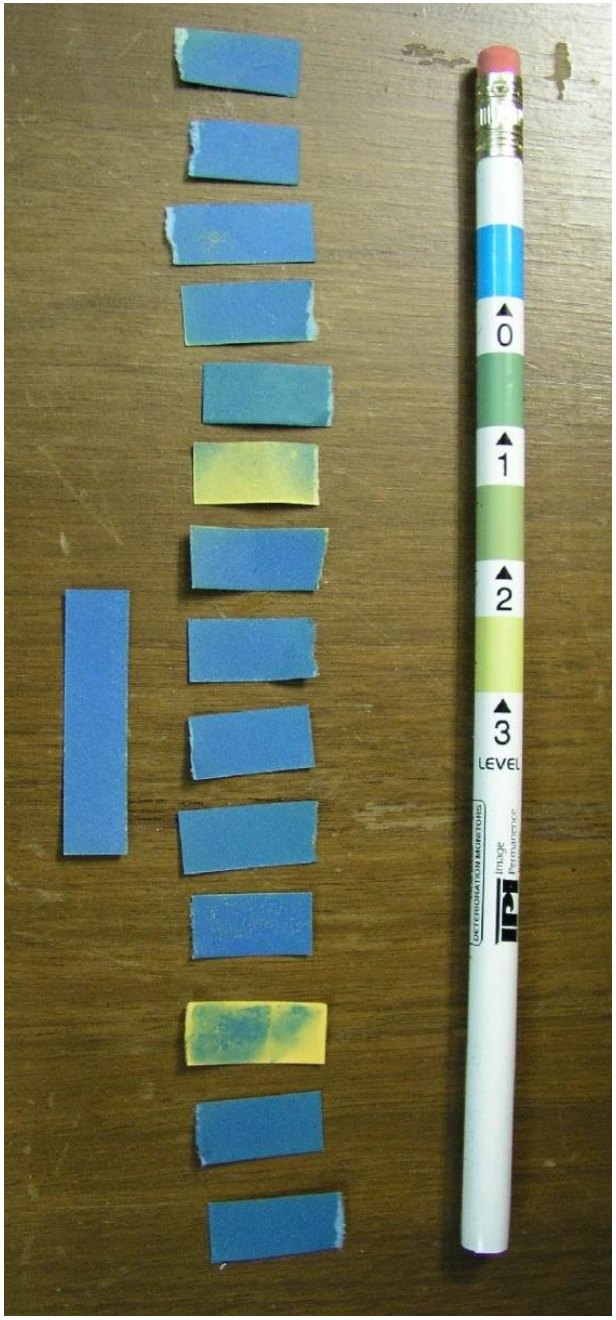
Scavengers?

- Used to recommend zeolites, activated charcoal, etc.
- May accelerate release of plasticizers and speed degradation
- But may be okay if plasticizer already lost!
- DO NOT USE! *Until further studies say otherwise*

Monitor!

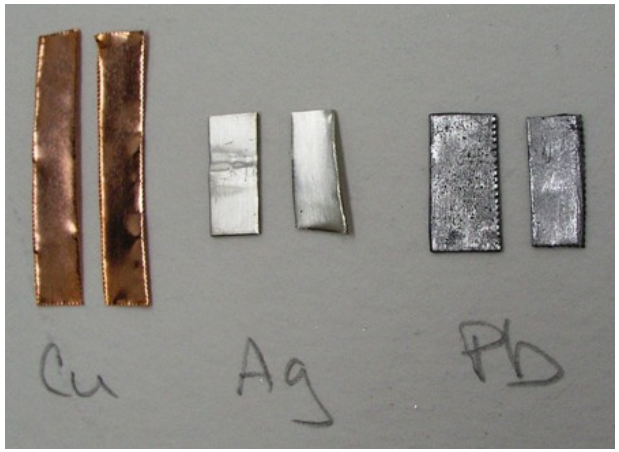
A-D Test Strips

- Developed by IPI for Cellulose Acetate film
- Reacts with acidic off-gas
- Monitor in dark in sealed, non-adsorbent container
- Not long-term monitor (1-2 weeks)



A-D Test Strips

Detecting Deterioration: Metal Coupons



Coupons in place with CN

Coupons after 1 week

Coupons after 2 weeks

LEFT: Cu coupon after 1 month exposure to off-gassing CN

RIGHT: Cu reference

Antoine Pevsner, *Portrait of Marcel Duchamp*, 1926.
Cellulose nitrate on copper with iron
Yale University Art Gallery

Handling

- Components may be toxic
- Always wear Nitrile gloves
- Cotton gloves are porous and often re-used so may spread toxins

Improve Labeling

- Avoid lacquer and adhesives
  - Solvents can accelerate deterioration
- Tie-on tags
- Soft pencil
- Label non-plastic

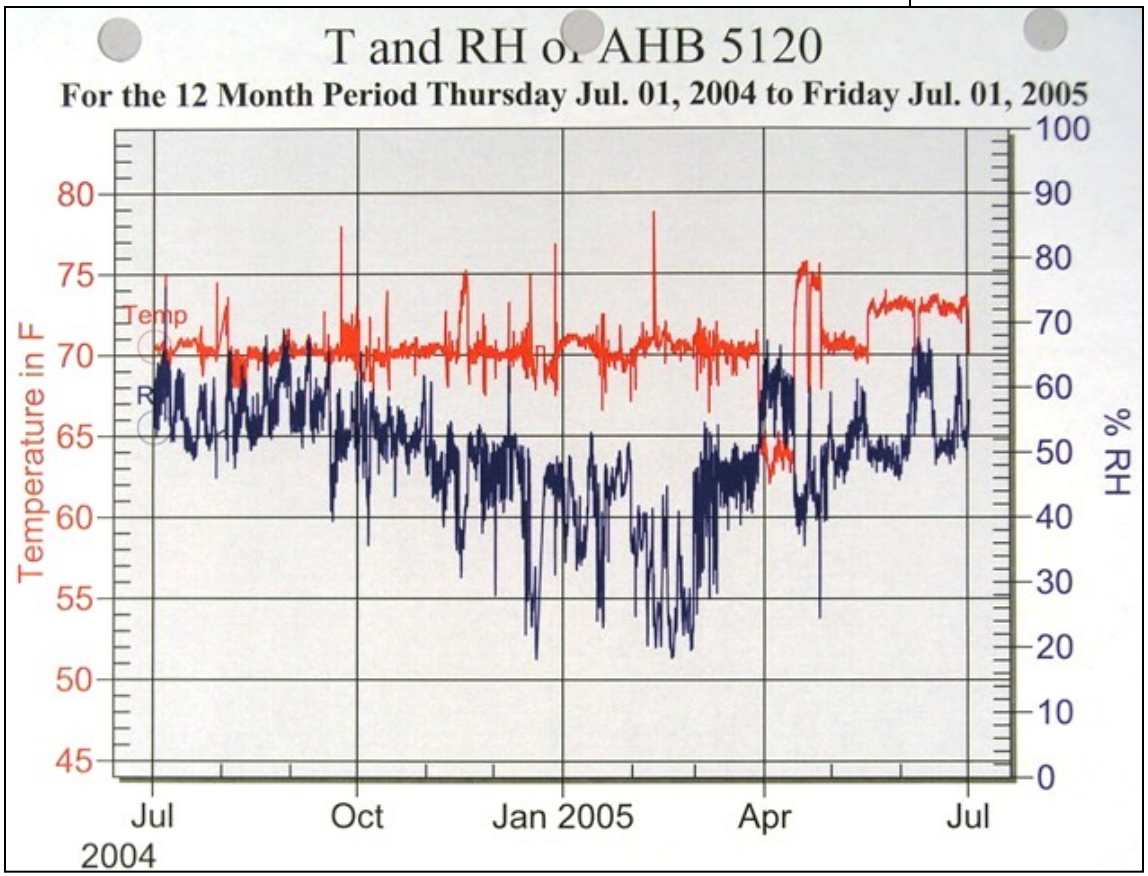
Improve Storage

CN Objects in PVC binder sleeves.

Improve Storage: T and RH

- Highest RH 65%
- Lowest RH 20%
- 20% RH changes

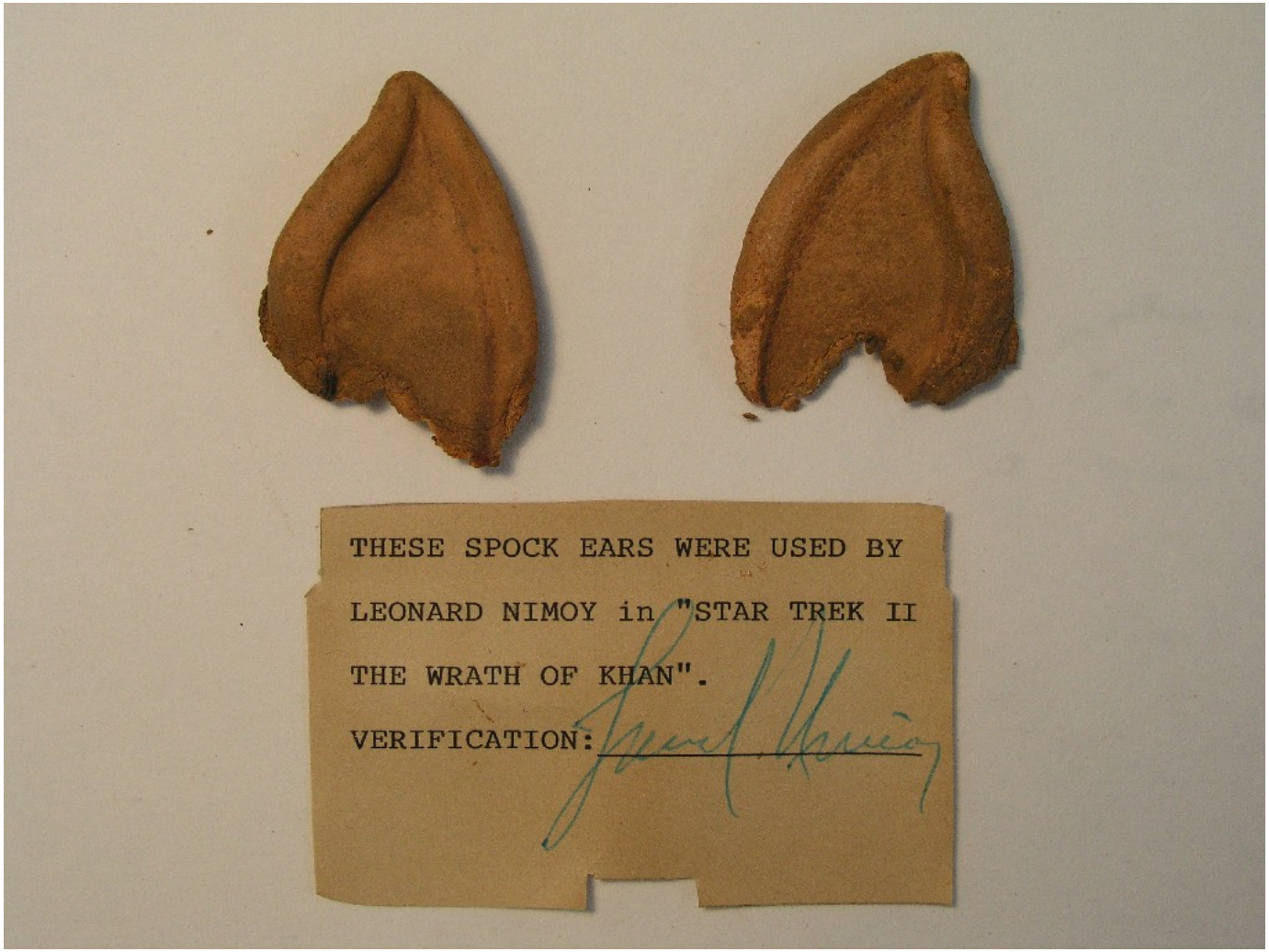
- T ranges 63-78°F



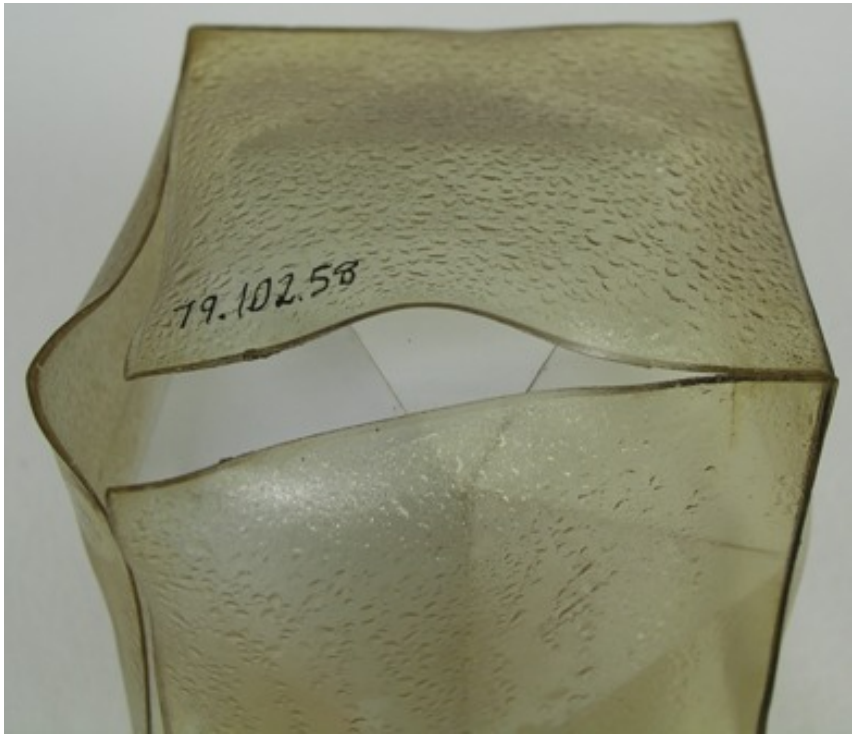
Low Temp Storage

- Chemical reactions reduced by 50% for 10°C (18°F) drop in T
- Ordinary Food Freezer is -20°C (-4°F)
- Become stiffer, brittle, shrink
- Insulate or double bag to prevent condensation
- Thicker may have dimensional changes - slowly acclimate each way
- Limits of space, size, cost and complex objects

Documentation



Deaccession



Preventive Approach

Step 1 – Observe

- Is the plastic weeping, crizzled, cracked, sticky, smelly, warped, discolored, crumbling, bloom?
  - If so, the plastic is likely deteriorating.
- Are other objects near the plastic corroded, covered in a film, or deteriorated in some way?
  - If so, the plastic may be deteriorating.
- Are the metal components of the cabinets or shelves corroded? Is there an acrid smell when you open the cabinet?
  - If so, the plastic may be deteriorating.

Preventive Approach

Step 2 – Confirm Observations

- **A-D strips**
- **Cresol Purple or Red** *(for Cellulose Nitrate)*
- **Metal coupons**
  - Silver
  - Copper
  - Lead

Preventive Approach

Step 3 – Separate

- If find off-gassing plastics, segregate them

Step 4 –Clean Former Storage Area

Step 5 – Consider the Environment

- Temperature
  - Degradation rate increases as T increases
  - Cool or cold storage

Preventive Approach

Step 5 – Consider the Environment (cont)

- RH
  - In general for plastics want RH 35% - 45%.
  - Fluctuations can cause warping and cracking.
  - RH below 25% can craze plastics
  - RH above 50% can start hydrolysis in some plastics with resulting acid formation and degradation

Preventive Approach

Step 5 – Consider the Environment (cont)

- Light
  - All light can damage
  - UV light can cause fading, color changes, start photo-oxidation degradation and cross-linking.
  - Keep plastics in the dark as much as possible
  - Recommended max level of 150 lux (about 15 footcandles) for exhibition

Preventive Approach

Step 5 – Consider the Environment (cont)

- Ventilation
  - Prevents build-up of gases but may loose plasticizers (PVC)

- Scavengers
  - Will become exhausted
  - Some may pull out plasticizers
  - *Not recommended as much anymore!*
  - Archival trays and boxes (blueboard) is good default

Preventive Approach

Step 6 – Support

- While plastic still pliable (esp. if shows signs of degradation) block in proper shape with stable non-adsorbent material (e.g. Tyvek)
- Remove stress
  - Stands to take weight off rubber tires
- Consider using silicone-release film barrier between stick plastic surface and support

Preventive Approach

Step 7 – Document

- Written and photographic documentation
- Once degradation starts, can be rapid
- Documentation may be all that can safely exist in collections

Step 8 – Deaccession

- May have to remove from collection

Preventive Approach Summary

Cellulose Nitrate

- Observe
- Monitor
- Ventilation?
- Scavengers?
- Stable environment
- Support
- Document
- Deaccession?

Interventive Conservation

POPART

Preservation Of Plastic ARTefacts in museum collections

- A consortium of EU research laboratories did a three-and-a-half year project on the study of plastics.
- Aim to develop strategies that improve the preservation and maintenance of plastics objects in museum collections.
- Recommended practices were established and risks associated for exhibiting, cleaning, protecting, and storing plastics were better identified.

- http://popart-highlights.mnhn.fr/

Interventive Conservation

POPART

Preservation Of Plastic ARTefacts in museum collections

- Cleaning study revealed ALL dry cleaning methods scratch plastics *(except compressed air*)
- Straight pass motion better than circular wiping
- Risk of solvent and wet cleaning *(call a conservator!)*

If dry clean*, may be safer *(based on less scratching)* to use:

- Synthetic leather chamois
- Cotton swab
- Paper tissue
- Feather duster
- Cleaning cloth for glasses
- Synthetic feather duster
- Leather chamois
- Sable hair brush
- Paper cloth
- Cotton cloth
- Compressed or canned air
- Microfiber cloth

** For aqueous cleaning, there is a different list*

Questions?