



Preservation Of Plastic ARTefacts in museum collections

DAMAGE ATLAS

Atlas of case studies
presenting typical damages



Project nbr 212218

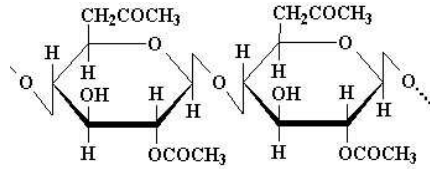
<http://popart.mnhn.fr>

Cellulose acetate (CA)

Categories

Semi-synthetic ; thermoplastic

Chemical structure



Production

- Cellulose acetate was created by Paul Schutzenberger in 1865, by acetylating cellulose under exposure of acetic acid, but manufacturing processes were not available before the first decade of the 20th century.
- as a stiff material, cellulose acetate needs to be plasticized. Triacetine or triphenyl phosphate and phthalates have been and are still used as plasticizers.
- Because of its low flammability, it tended to replace cellulose nitrate as a “safety” material for many uses.
- spinning methods were also developed before the outbreak of WWI for creating artificial silk and a wide range of textile fibers

Forms and applications

- All type of objects imitating natural materials, like tortoiseshell, horn, ivory or mother-of-pearl. It is still very present in glasses manufacturing.
- other cast objects, such as Lego® bricks (before 1965)
- flexible sheet for photographic “safety films” and other types of uses
- wide range of textile fibers

Some trade names

Rhodoid®, Viscose®, Rayon®, Tricel®

Physical characteristics and appearance

- Highly transparent material
- Raw cellulose acetate is a rigid material which requires plasticizers.
- Its scratching resistance is high.
- CA is soluble in water, alcohol, ketone and chlorinated solvents.

Degradation process

- Higher water absorption.
- Hydrolysis in presence of acids and moisture.
- CA emits acetic acid (smell of vinegar), which corrodes metals and causes autocatalytic degradations.
- Loss of plasticizer leads to shrinkage and warping.

Degradation factors

Moisture, light, heat ; ventilation or containment may influence the degradation processes.

- Damage illustrated

A: warping, shrinkage

B: sweating

C: bloom

D: blister

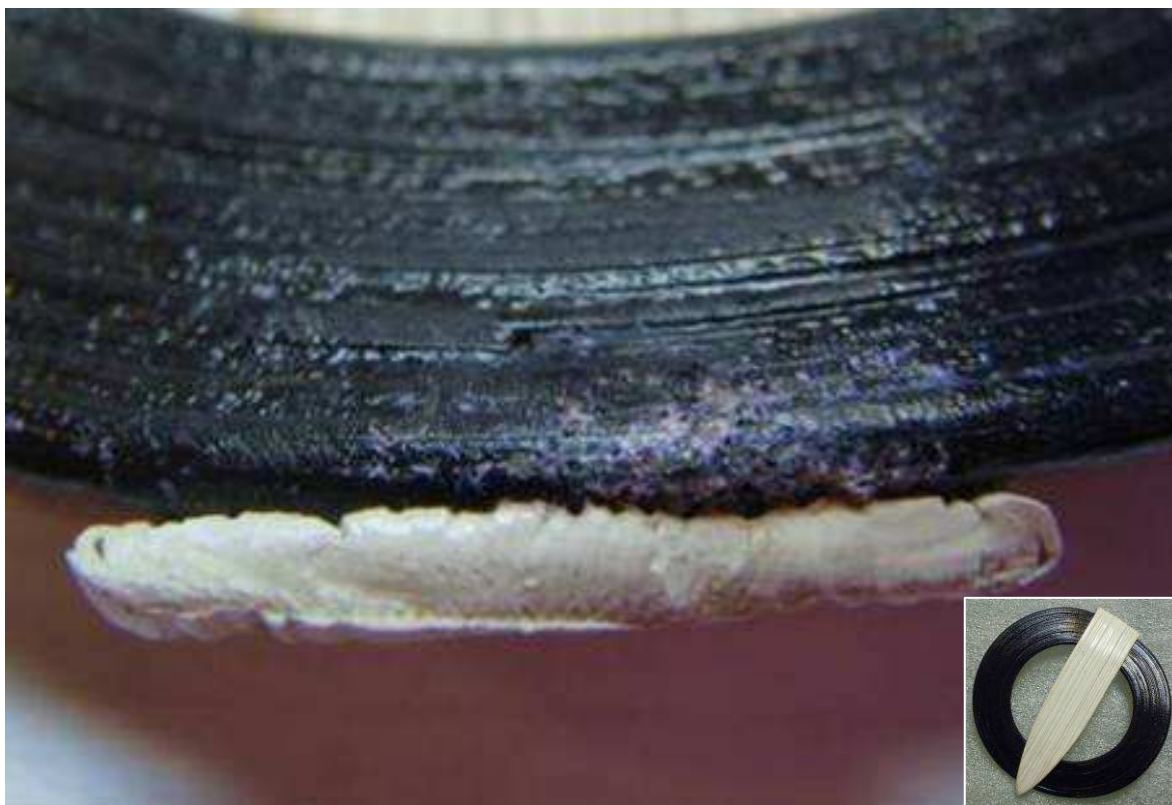
E: corrosion of metallic elements

- Not illustrated

F: vinegar smell (acetic acid off-gassing)



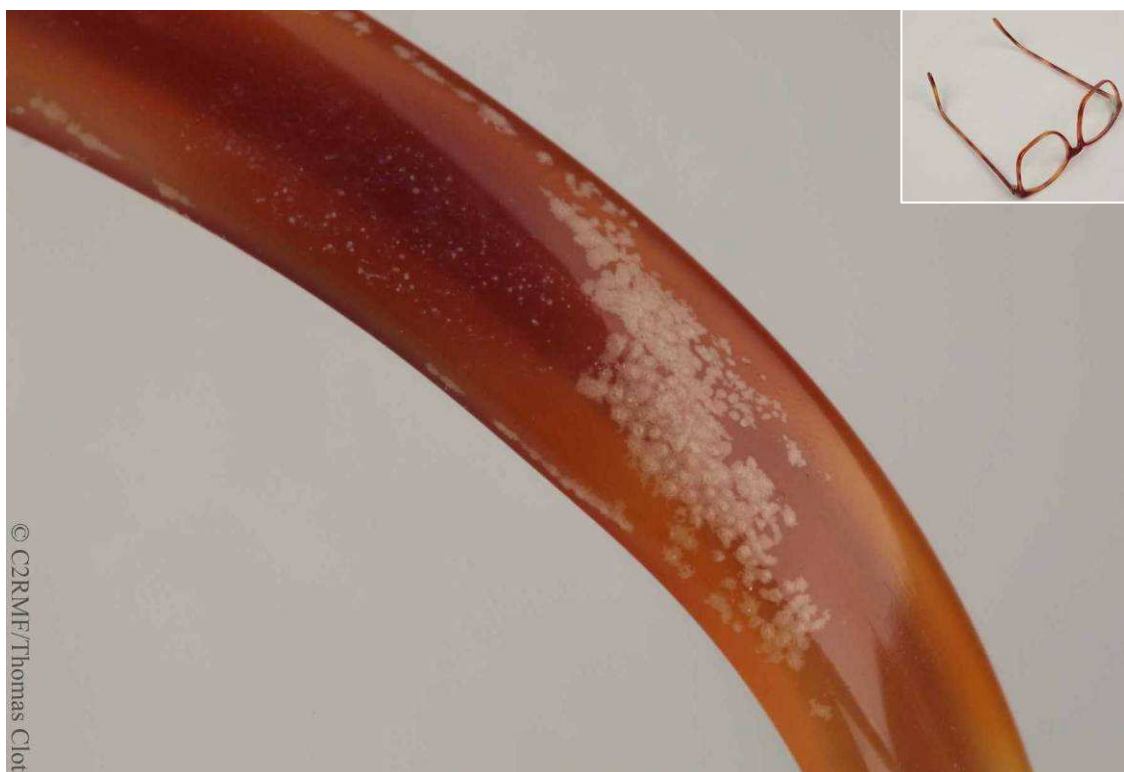
A – Purse (1920s) : *warping , shrinkage*
© C2RMF



B – buckle : *sweating* (migration of plasticizers)
© C2RMF



C– toys, figurines (early 1960s): *bloom* (solid residues from plasticizer exudation)
© C2RMF



© C2RMF/Thomas Clot

D - Glasses: *blister*
© C2RMF



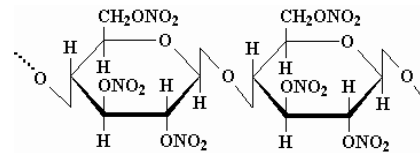
E - Glasses : corrosion of metallic elements
© C2RMF

Cellulose Nitrate (CN)

Categories

Semi-synthetic ; thermoplastic

Chemical structure



Production

- **Cellulose Nitrate** was synthesized by Christian Schönbein in 1846, by nitrating natural cellulose through exposure to nitric acid. Pure cellulose nitrate is a powerful explosive but is not suitable for moulding.

- **Celluloid** is seen as the first "plastic". It is a mixture of **cellulose nitrate plasticized with camphor** which makes the compound available for commercial applications. Different processes were developed and patented between 1862 (Alexander Parkes) and 1870 (John W. Hyatt).

Celluloid has been extensively produced as a versatile material from the end of the 19th century but was progressively replaced by newer plastics in the interwar period, because of its high flammability and its bad chemical stability.

Forms and applications

in the form of casts or plates, Celluloid was a common substitute for natural materials, like tortoiseshell, horn, ivory or mother-of-pearl. It was also used in the making of toys and dolls

In the form of flexible sheets, it has been extensively used in the making of early photographic films

Some trade names

Celluloid[®], Parkesine[®]

Physical characteristics and appearance

- Cellulose nitrate is transparent
- Cellulose nitrate is highly flammable, especially in the form of sheet.
- Cellulose nitrate is a rigid material which requires plasticizers.

Early in the 1920s phthalates began to replace camphor as plasticizers, triphenyl and tricresyl phosphates were also used after World War II. Mineral fillers like titanium oxide can help to stabilise the material.

.soluble in ketones, ether and ester solvents

Degradation process

- High water absorption.
- Hydrolysis in presence of acids and moisture.
- CN produces corrosive nitric acid (acid smell), which corrodes metals and causes autocatalytic degradations
- Migration of plasticizers induces shrinkage and warping.

Degradation factors

Moisture, light, heat ; ventilation or contained environment may influence the degradation

Damage illustrated***A: crazing******B: crack******C: bloom******D: sweating******E: become brittle******F: become crumbly******G: yellowing******H: corrosion of metallic elements
in the vicinity of degraded CN******I: acrid and/or camphor smell***



A – Hair slide, tortoiseshell imitation : *crazing*, associated damage : *loss of transparency*
© C2RMF



B – Comb (horn imitation): *crack*
© C2RMF



C – Comb : *bloom* (solid deposit made of exuded and dried plasticizer)
associated with *loss of transparency, change in gloss and crack* © C2RMF



D – detail of glasses : *Sweating*
(liquid plasticizer exuding in the form of drops)
© C2RMF



E – Comb (tortoiseshell imitation): *Material become brittle*
© C2RMF



F – Comb : *Material become crumbly*
© C2RMF

G - Doll (trade mark Petitcollin):
Yellowing
 © C2RMF



H- Glasses : Corrosion of metallic element
(copper alloy)
 © C2RMF



I- Odour of degrading Celluloid :

- **Camphor** (loss of plasticizer)
- **Acrid** (nitric acid off-gassing), generally associated with oxidation of materials in the vicinity.

Above : a tissue paper wrapping degraded by CN combs

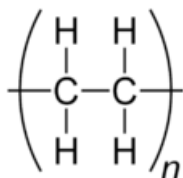
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Polyethylene (PE)




Categories
Synthetic, thermoplastic

Chemical structure




a linear molecule of polyethylene (HDPE)


a branched molecule of polyethylene (LDPE)

Production

In 1935, by working with ethylene at high pressure chemists generated a solid form of polyethylene. LDPE was first used during World War II by the British army for insulating radar cables. In 1953, Karl Ziegler invented high-density polyethylene (HDPE) which was used first for pipe manufacturing

Forms and applications

Cast: food containers (like Tupperware®), toys, plastic flowers, garbage bins, squeeze bottle, irrigation tube
Sheet: packaging film, black mulch film, garbage bag, food bag, zip-lock bag (Minigrip®)
Foam : Rigid or soft

Some trade names

Ethafoam®, **Ethylux®**, **Plastazote®**

Physical characteristics and appearance

chains length, branching off the main chain and type of side chains determine the mechanical properties of the material, such as density, stiffness, tensile strength, flexibility, hardness, brittleness, elongation.

- HDPE (High Density Polyethylene) is hard to semi-flexible, waxy surface, opaque
- LDPE (Low Density Polyethylene) is soft, flexible, waxy surface, translucent.

Though PE is opaque, it may be transparent in the form of film or thin sheet.

PE is easy to mold and shape.

PE is solvents acids and basics resistant but can swell in aliphatic and aromatic hydrocarbon

Degradation process

Oxidation and photo-oxidation.

Degradation factors

Oxygen, light, heat

PE sheets may be oxo-degraded during the manufacturing process for a better bio-degradation

Damage illustrated

A: *tear associated with fold*

B: *crazing*

C: *become brittle*

Not illustrated

D: *smell of paraffin*



A - Disposable umbrella (1980s) : *Fold and tear*

© C2RMF



B - Beaker (Tupperware®) : crazing
© C2RMF



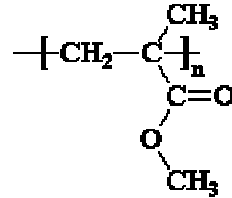
C - Strainer : become brittle
© RCE

Poly methyl methacrylate (PMMA)

Categories

Synthetic, thermoplastic

Chemical structure



production date

The process to form polymethyl methacrylate (PMMA) from methyl methacrylate was found in the 1870s. However it was not patented before the early 1930s by Otto Röhm under the brand name Plexiglas®.

It found rapid and important commercial applications in glazing.

Some trade names

Altuglas®, **Lucite®**, **Plexiglas®**, **Perspex®**

Forms and applications

Plate: all types of glazing , billboards, furniture, etc

Cast : jewelry, vessel, etc.

Physical characteristics and appearance

PMMA is transparent, hard and rigid

Its impact resistance is medium and it is highly sensitive to scratch and abrasion

PMMA is hygroscopic ; it is very sensitive to many solvents (ketone, alcohol, hydrocarbon...) and more resistant to acids and bases.

Degradation process

- Water absorption leads to chemical break down resulting in crazing and loss of transparency.

Degradation factors

Moisture, light, heat

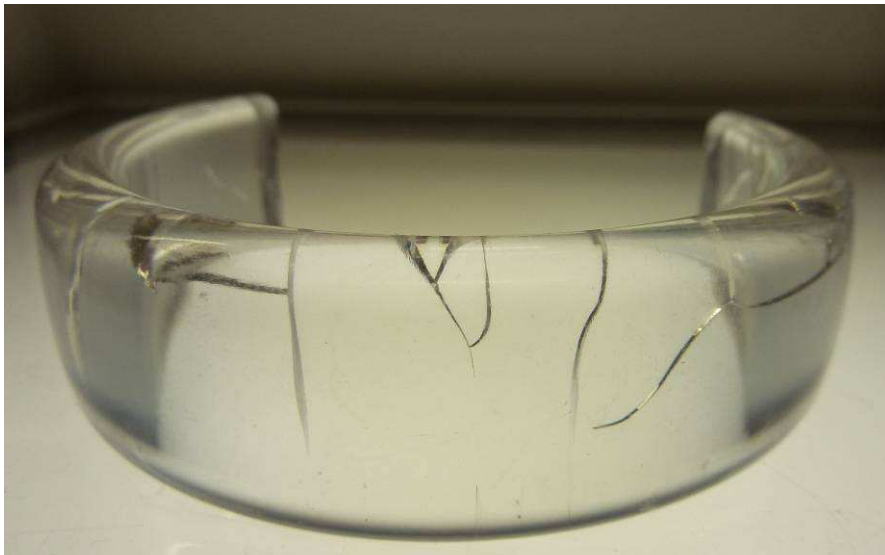
Damage illustrated

A: crack

B: crazing

C: scratch and abrasion

Associated degradations : *loss of transparency, change in gloss*



C- Bracelet : crack - © RCE



B- Salad bowl : *crazing*, causing a loss of transparency - © RCE



C- Transparent plate : *Scratch and abrasion*, causing a loss of transparency and change in gloss - © C2RMF

Polyurethane ether (PUR ether)
Polyurethane ester (PUR ester)

Categories

Synthetic ; thermoplastic, thermoset or elastomer, depending on formulation

Chemical structure

- Large family of materials formed by reaction of polyols with poly-isocyanates.
- Polyurethanes ester are made from polyester polyols ; polyurethanes ether from polyether polyols.

Production

- Otto Bayer discovered and patented PUR for IG Farben in 1937.
- Mass production of flexible PUR foams started in 1954 and developed from the 1960s onwards ; PUR ether have largely replaced PUR ester in the flexible urethane foam industry, but some applications still exist.
- Lycra® fibre was created in 1958 by DuPont.

Forms and applications

PUR is produced in different forms: coatings, fibres, flexible foams and cross-linked foams

- Thermoplastics :fake leather and textile coatings
- Thermosets: flexible and rigid foams
- PUR rubbers:, moulded objects, floor covering, wheels

Some trade names

Bayflex® , Elastane® , Lycra® , Spandex®

Physical characteristics and appearance

PUR are non-transparent plastics.

They can be hard or flexible, their impact resistance is high and they are resistant to scratch.

PURs are sensitive to alcohol and ketone solvents.

Degradation process

PUR ether : oxidation and photo-oxidation.

PUR ester : hydrolysis, oxidation and photo-oxidation

Photo-oxidation is oxidation of the PUR surface in presence of oxygen or ozone that is facilitated by ultraviolet radiations and daylight.

Photo-oxidation causes yellowing. Once begun, the phenomenon still progresses, even in the dark.

Oxidation and photo-oxidation cause a reduction of molecular weight that coincides with a loss of mechanical properties (PUR hardens then becomes brittle and crumbly). Foams deteriorate much faster due to the larger extent of material exposed to environment

Degradation factors

PUR ether: **light**, heat

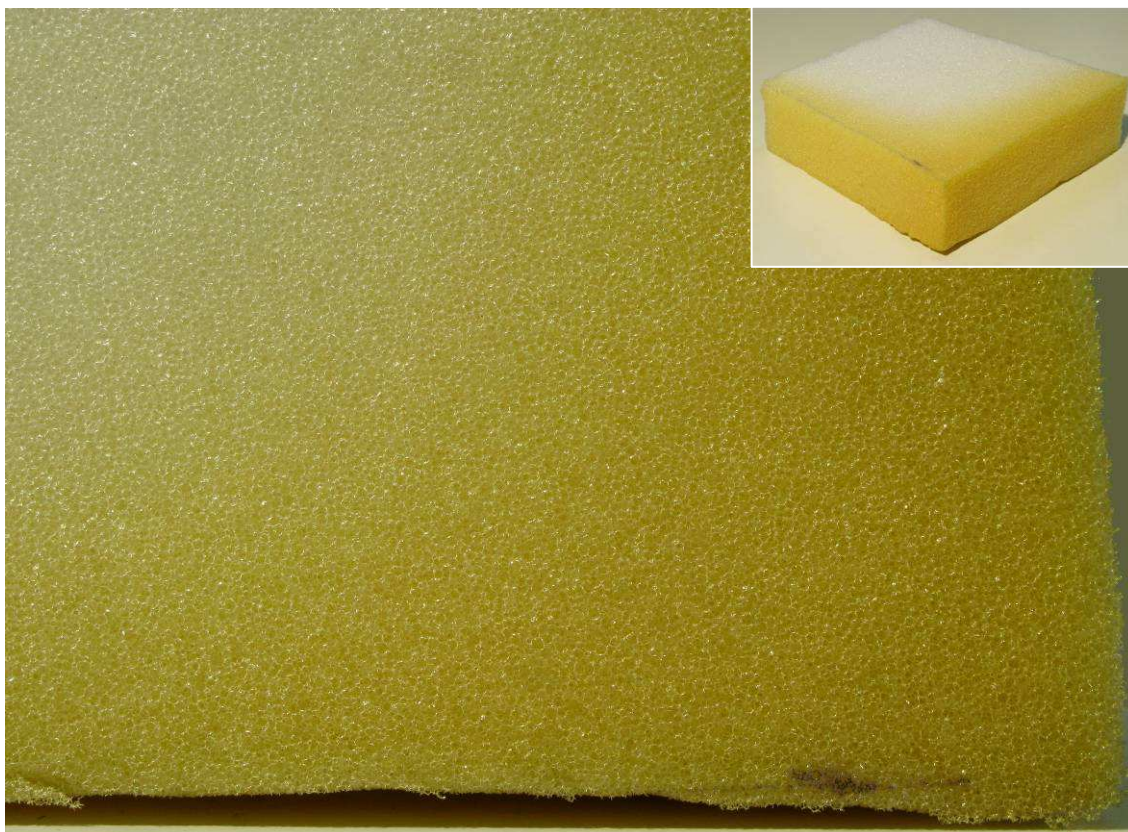
PUR ester: **moisture**, light, heat

Damage illustrated :

A : yellowing

B : become brittle and crumbly

C : bloom



A- Flexible PUR ether foam (2000s): *yellowing* (from edges exposed to light)
© C2RMF



B – suitcase cushioning (1970s): PUR ester foam become *brittle* and *crumbly*
© C2RMF



3 - Suitcase coated with leatherette (1960s) : *bloom* (unzipped polymers of PUR ester)
© C2RMF

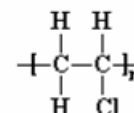
Polyvinyl chloride (PVC)



Categories

Synthetic, thermoplastic

Chemical structure



Production

Polyvinyl chloride was discovered during the 19th century when gas vinyl chloride exposed to sunlight resulted in an off-white solid material. But this raw material was unsuitable for any industrial application. In the 1920s the way to plasticize PVC was found. PVC achieved then a widespread commercial use.

Phthalates of different types are the most common plasticizers but some of them are progressively banned for their health effects.

Some trade names

Excelon[®], Tedlar[®], Trovicel[®], Tygon[®], Verilon[®]

Forms and applications

UPVC: toy, plumbing pipe, electrical conduit, window frame, rigid panels blister pack, clear bottle

PPVC: Plasticized PVC is available in the form of sheet, plate, foam and cast toys, clothing, fake leather, waterproof coatings (table-cloth and shower curtain), inflatable structures, non-food bottle, garden hose, shoe sole, cable insulation, medicine accessories, watch strap, tape, etc..

Physical characteristics and appearance

- Unplasticized PVC is hard and rigid (UPVC)
- Plasticized PVC is flexible and elastic (PPVC)

Polyvinylchloride is generally transparent with a bluish tint and can be colored and opacified. It is sensitive to many solvents: ketone, ester, aromatics and chlorinated hydrocarbon solvents but resistant to oils.

Degradation process

Plasticizers migration results in sweating at the surface and in hardening and shrinkage. A too important ventilation accelerates the phenomenon.

Under high heat and light, hydrochloric gas may escape from PVC.

PVC becomes yellow and darker as dehydrochlorination progresses.

Degradation factors

Light, heat ; ventilation or containment may influence the degradation processes.

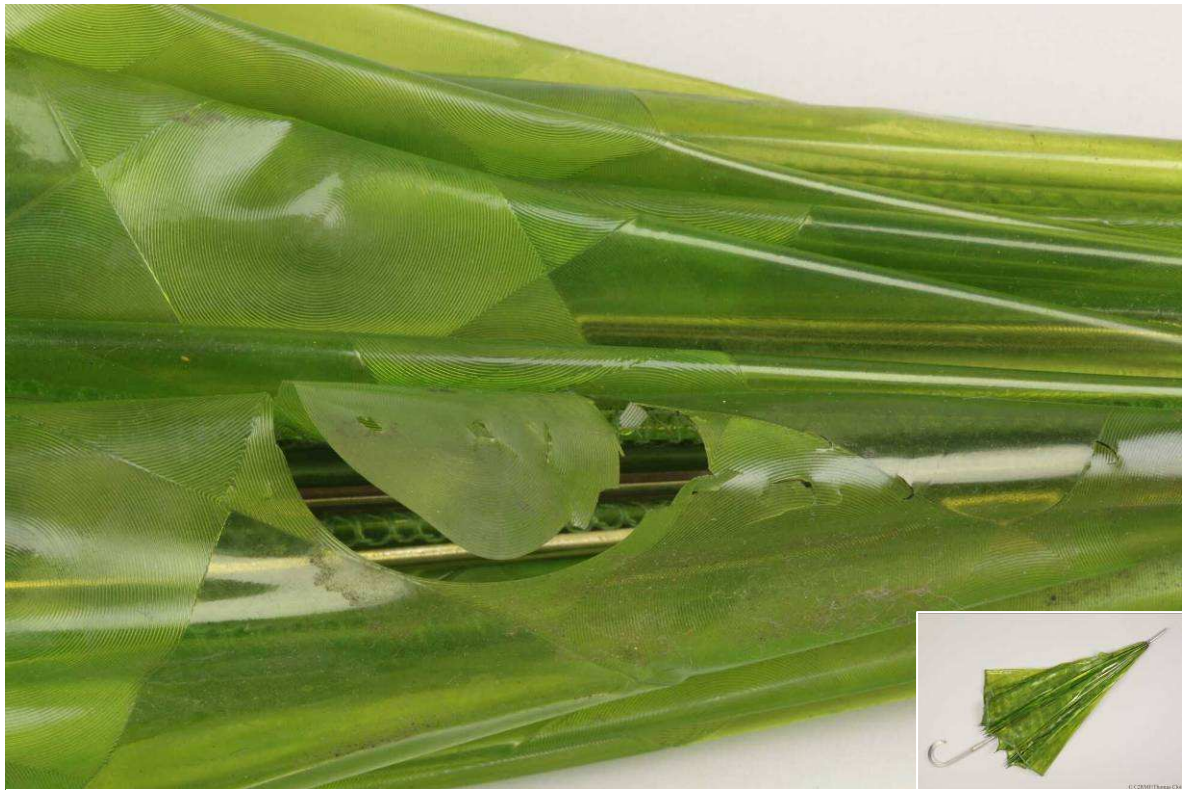
Damage illustrated (Plasticized PVC only) :

A: tear

B: sweating

C: yellowing

D: shrinkage



A - Umbrella (1979) : tear
© C2RMF



B- Raincoat (1978) : - sweating of phtalates plasticizers in the form of drop
- sticky surface

© C2RMF



C – Purse handle, embroidery covered with a PPVC sheet : *yellowing*
© RCF



D- Chair, metal, melamine formaldehyde resin (Formica®) and PVC (1960) : *shrinkage* of the black PVC strip (© C2RMF)