Consolidation of artefacts by gamma irradiation

IAEA - TECHNICAL COOPERATION DEPARTMENT
Division for Europe
Project RER 8015

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1.Radiation-curing monomers and resins

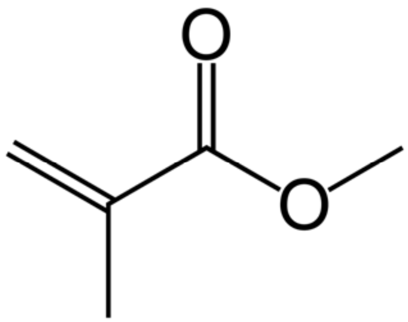
2. Mechanism of radiation-polymerization

3. Impregnation process of porous artefacts

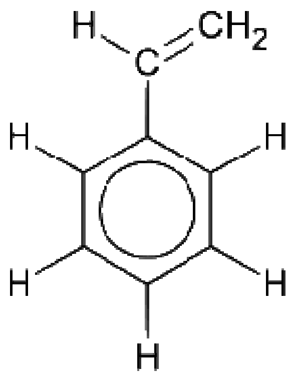
4. Irradiation of impregnated artefacts

5. Some recent treatments

Radiation-curing monomers

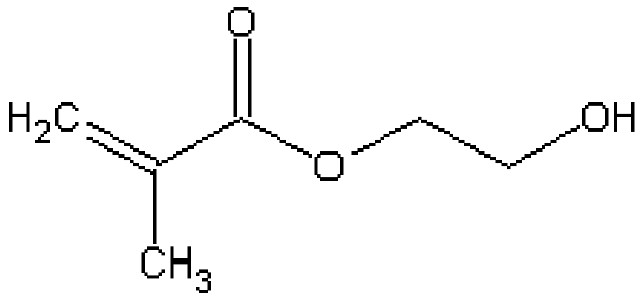


Methyl methacrylate

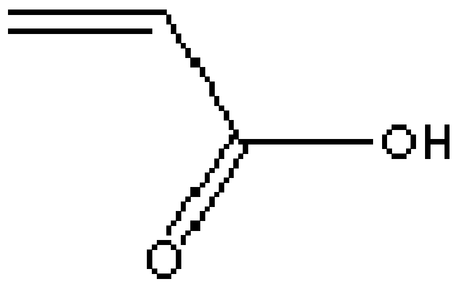


Styrene

Water soluble monomers

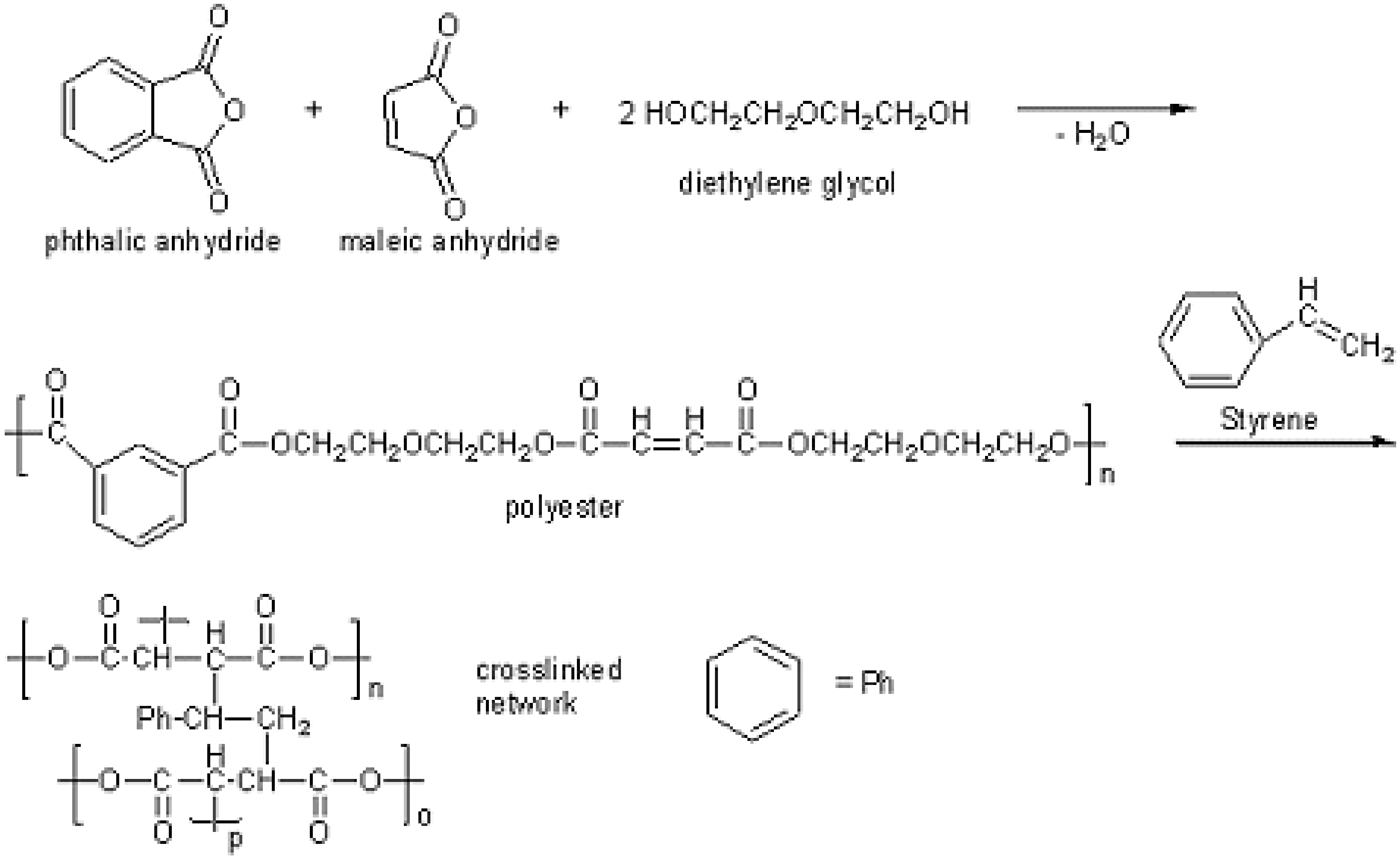


Hydroxy-ethyl-methacrylate

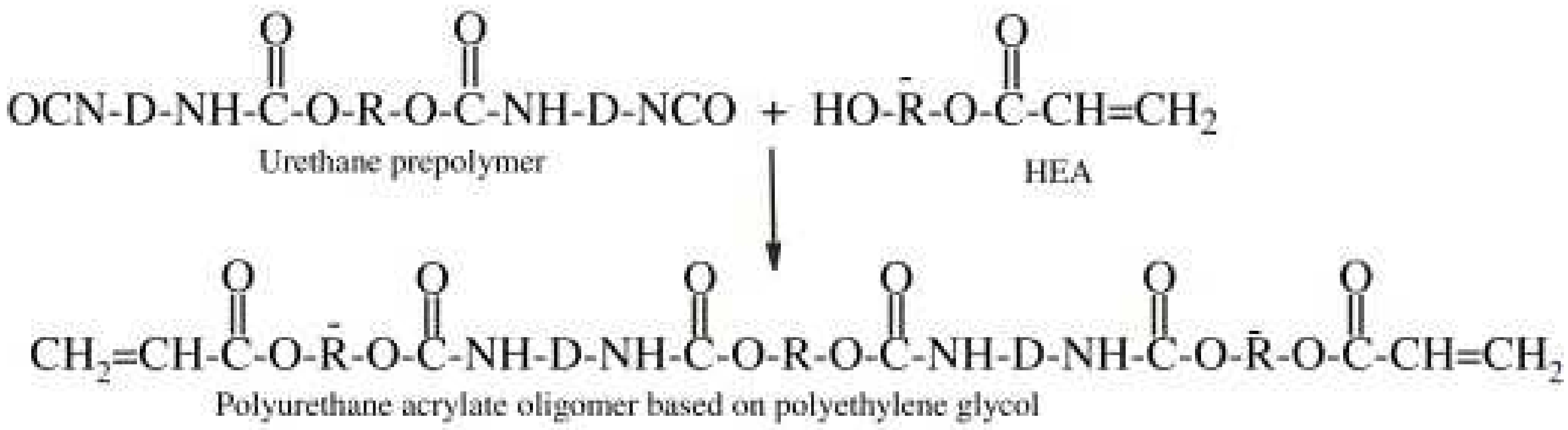


Acrylic acid

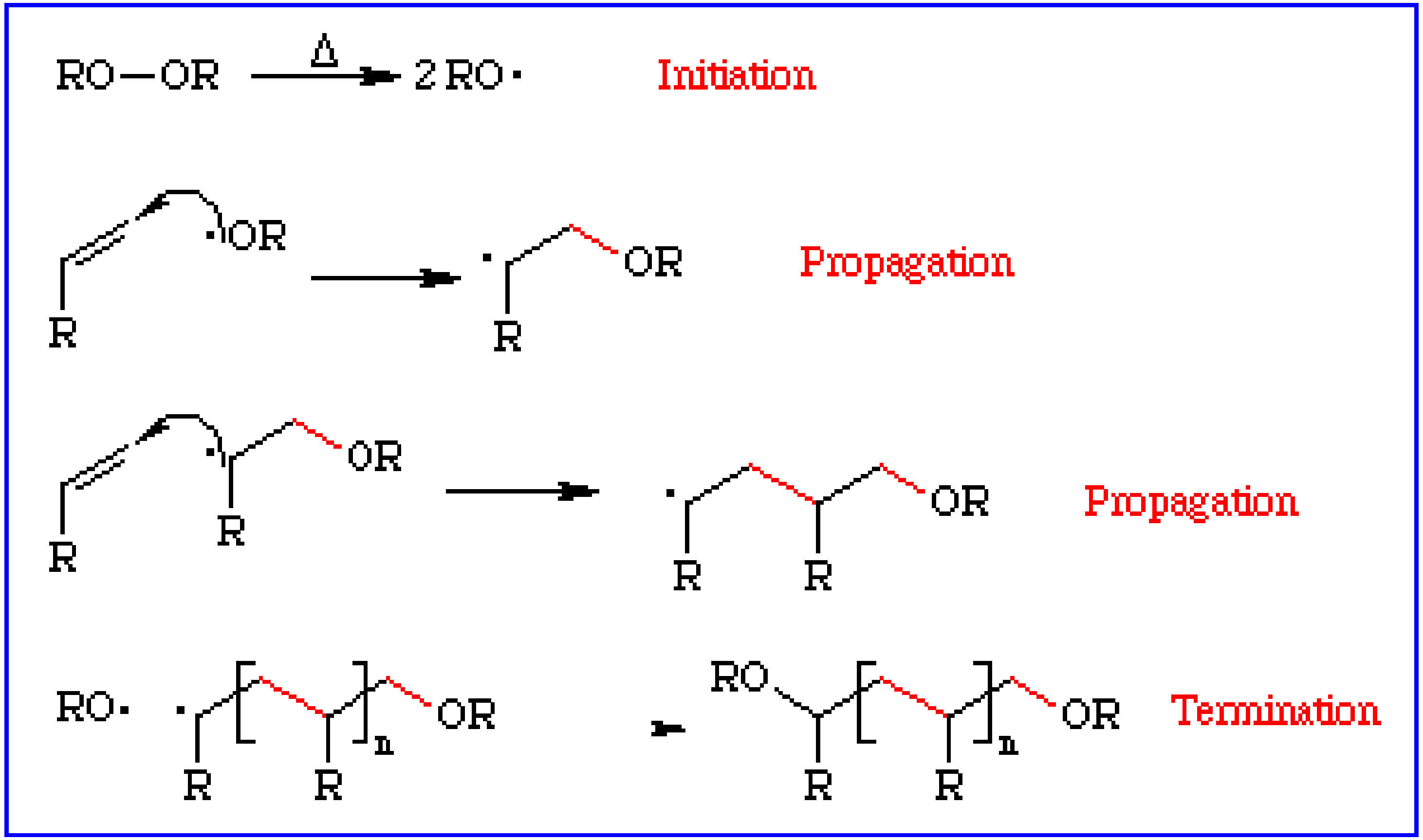
Unsaturated polyester resin



Diacrylate oligomer for UV or E-beam curing



Where $\bar{R}$ = $-CH_2-CH_2-$



Free radical polymerization initiated by peroxydes,
Formation of linear polymers, thermoplastic type

Free radical polymerization initiated by Radiation

Monomer + hv ⟶ M^* excited state

M* gives free radicals M°

Same kinetics : initiation , propagation and termination

But Initiation by radiation : No activation energy necessary

while Initiation by Thermal Catalysis : 25-30 kcal /mole

Overall activation energy E :

$E_{radiation}$ = 6 kcal/mole

$E_{chemical}$ = 20 kcal/mole

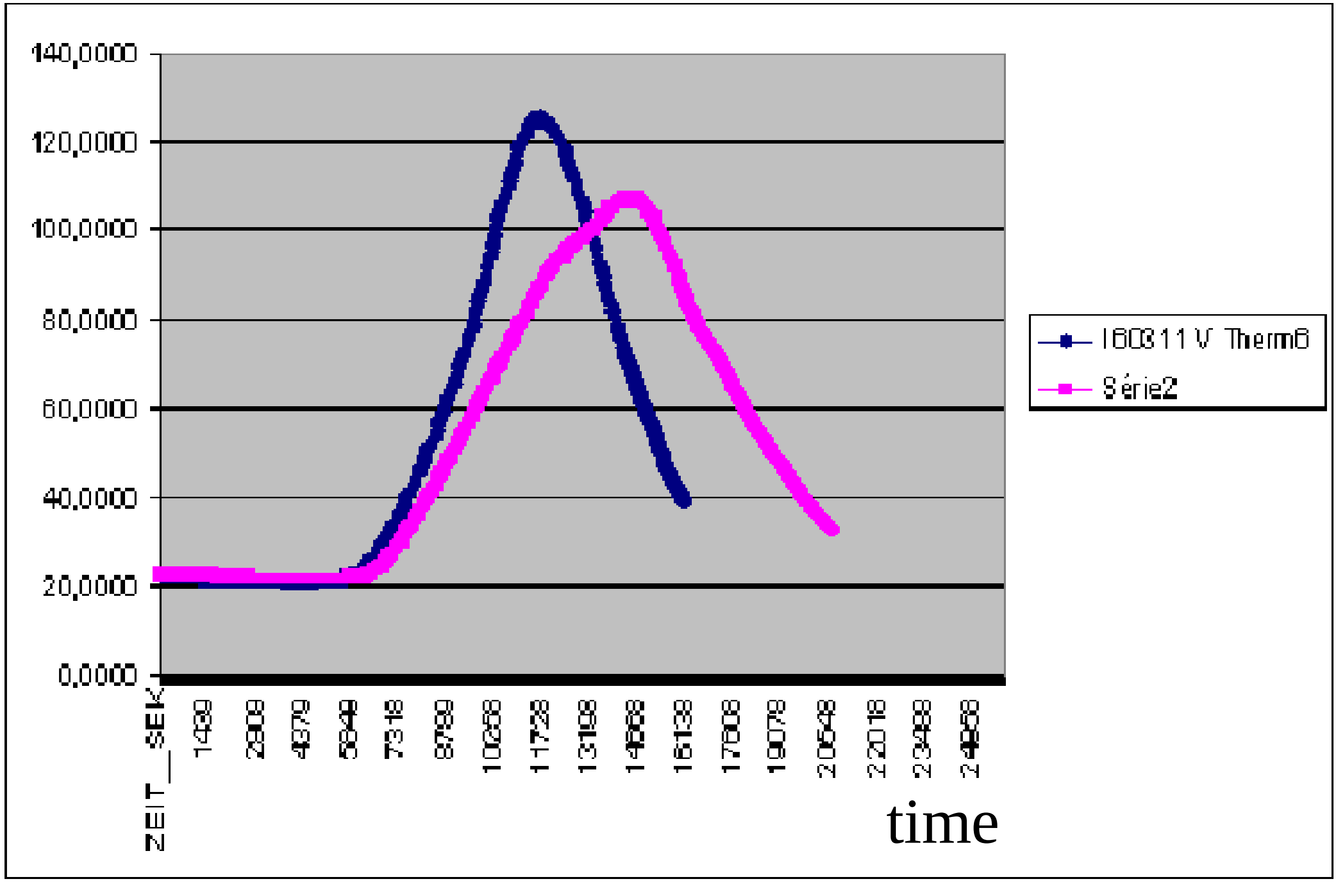
Less heat dependance of the radiation rate of polymerization

Rate of polymerization R: $\boldsymbol{R = k \times I^{1/2}}$

where I is the dose rate

Heat build-up in the resin during radiation-curing, depending on the dose rate, the « **Gel effect** »

temperature



The « ***G*** **value** » : radiation-chemical yield, total number of free radicals produced per 100 eV

- Gr for methyl methacrylate: 11.5 radicals per 100 eV
- Gr for styrene : 0.69

The « **Gel Effect** » :

1. first phase : constant rate of polymerization
2. After a certain conversion, important increase of the overall rate
   Increase of molecular weight of the resulting polymer
   Overheating of the solution!
   Reasons : accelerated propagation rate or a reduced termination rate
   Growing polymer chains are trapped in the gel-like phase and termination between 2 active chains become impossible owing to the lack of mobility of the polymer chains

Main advantages of radiation-curing :

- Initiation of free radicals independent of the temperature

- Stop free radicals formation by interruption of irradiation

- No chemical residue from catalysts

- The resin can be reused for further impregnation, owing to the absence of chemical catalyst

- During irradiation with low dose-rate : much less heat build –up and higher degree of polymerization

- Much more complete and homogeneous polymerization thanks to the penetrating radiation : less than 1 % of monomer residual after curing

•First application of conservation of cultural heritage item, 1970

Consolidation by methyl methacrylate polymer (Plexiglass)

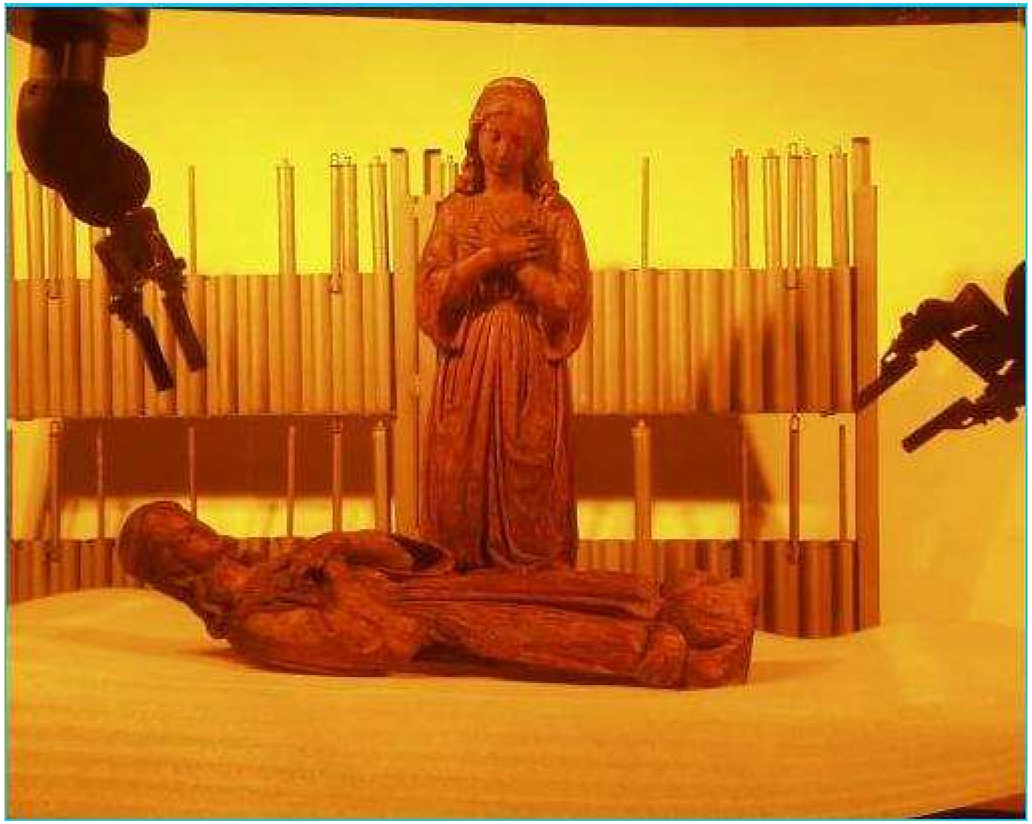
Ceremony 41 years later, September 2011

Hôtel Lesdiguière Parquet

41 years later, September 2011

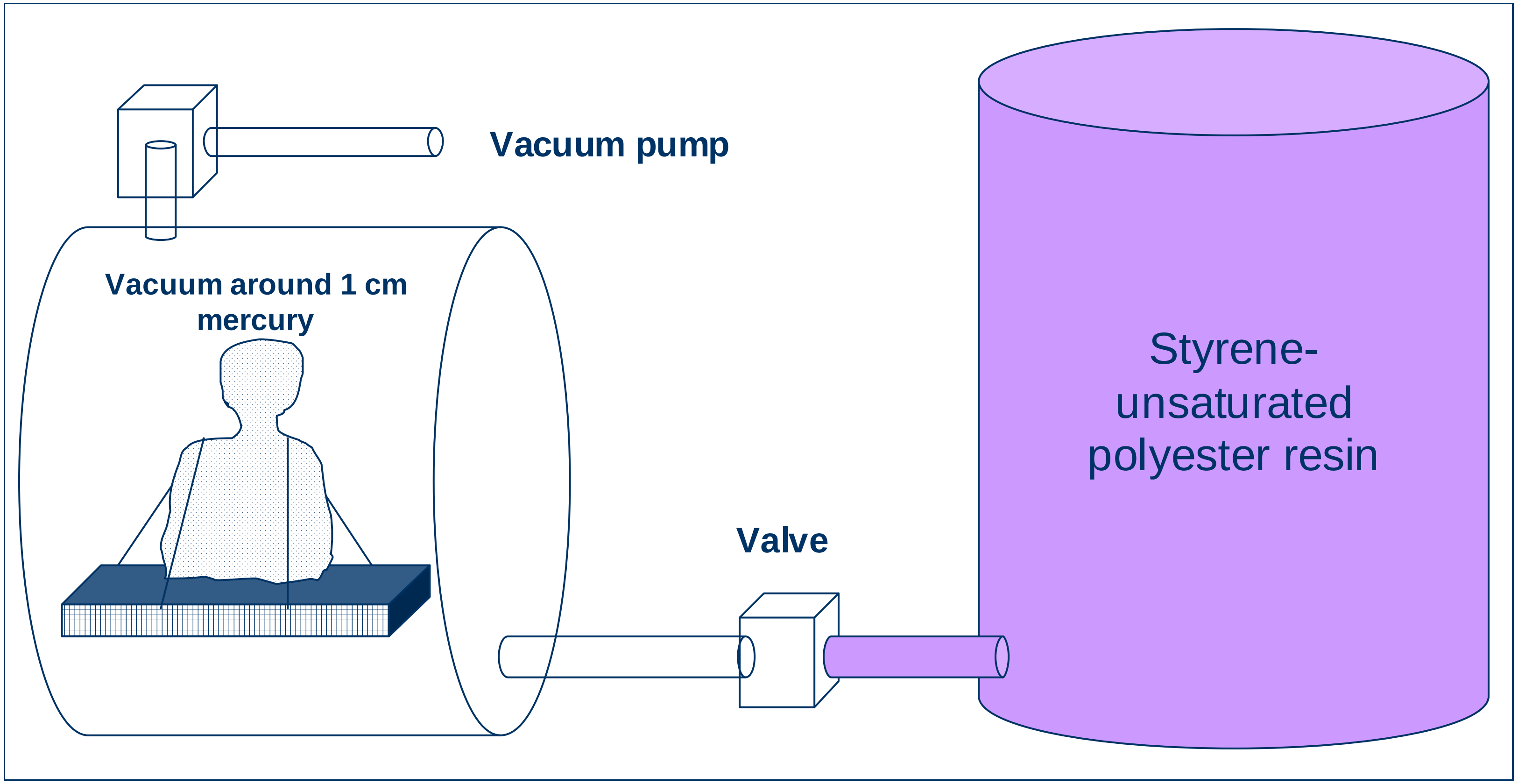
Dry porous “Nucléart” consolidation

- Gamma irradiation process for dry wood (or other porous material) consolidation by impregnation with radiation-curing resin
- Vacuum pressure impregnation of *unsaturated polyester-styrene* resin
- Crosslinking-controlled thanks to irradiation



Impregnation of dry porous material in 4 steps

- 1st step

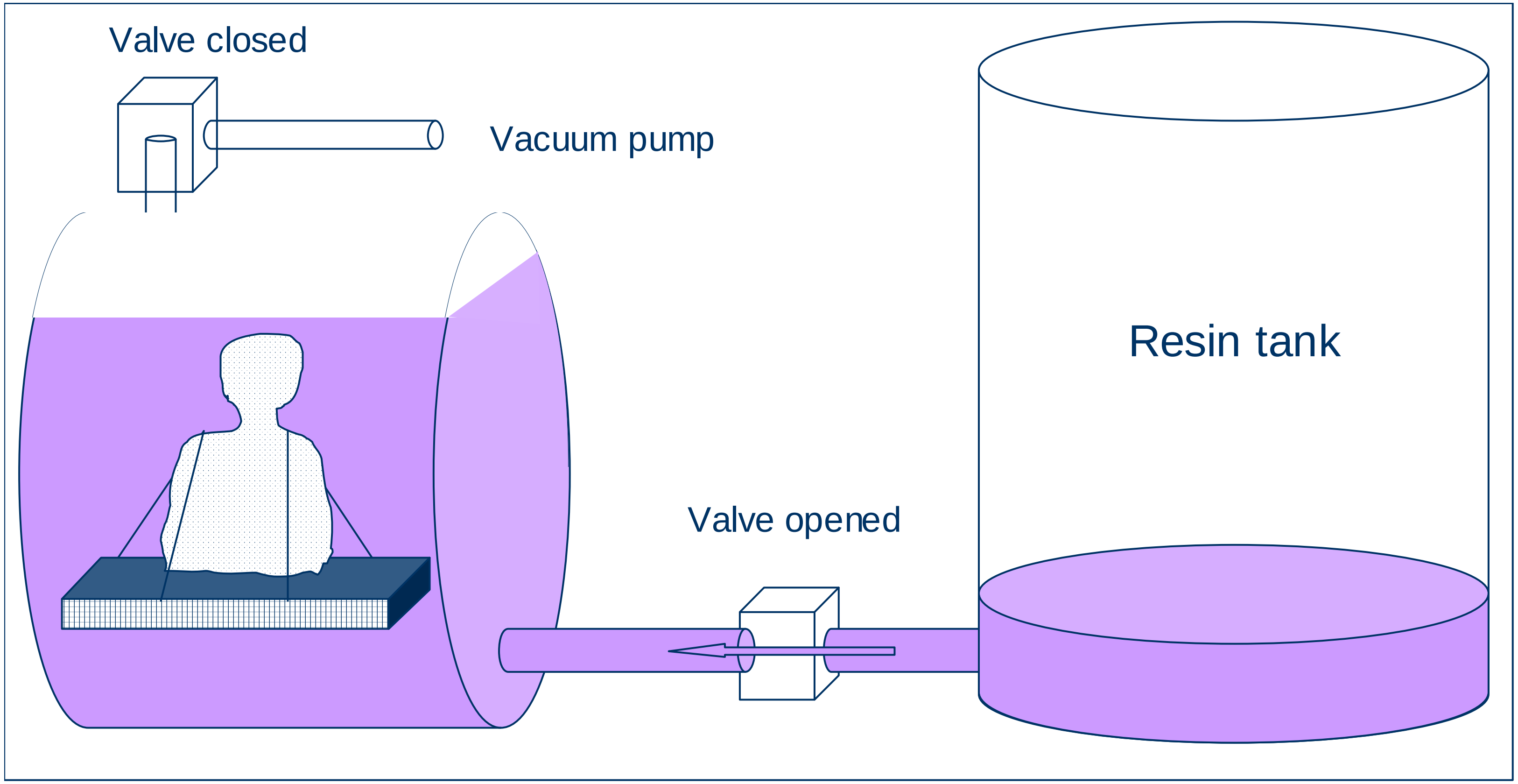


Object in the tank under vacuum,

Resin in the storage tank. Duration of this phase : 8 to 16 hours

Impregnation of dry porous material

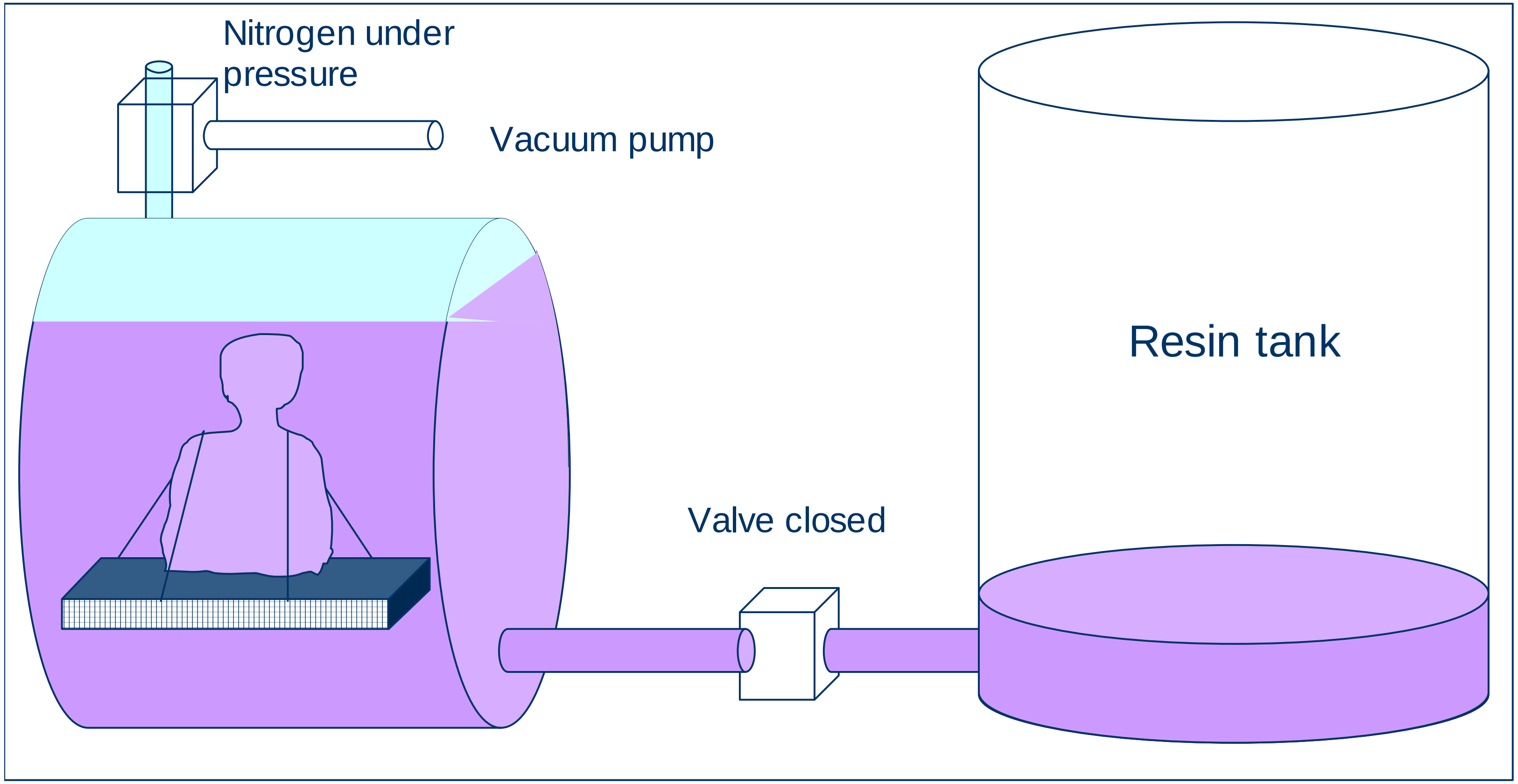
- 2nd step



The impregnation tank is filled by the resin from the storage tank. Total immersion of the artefact in the resin

Impregnation of dry porous material

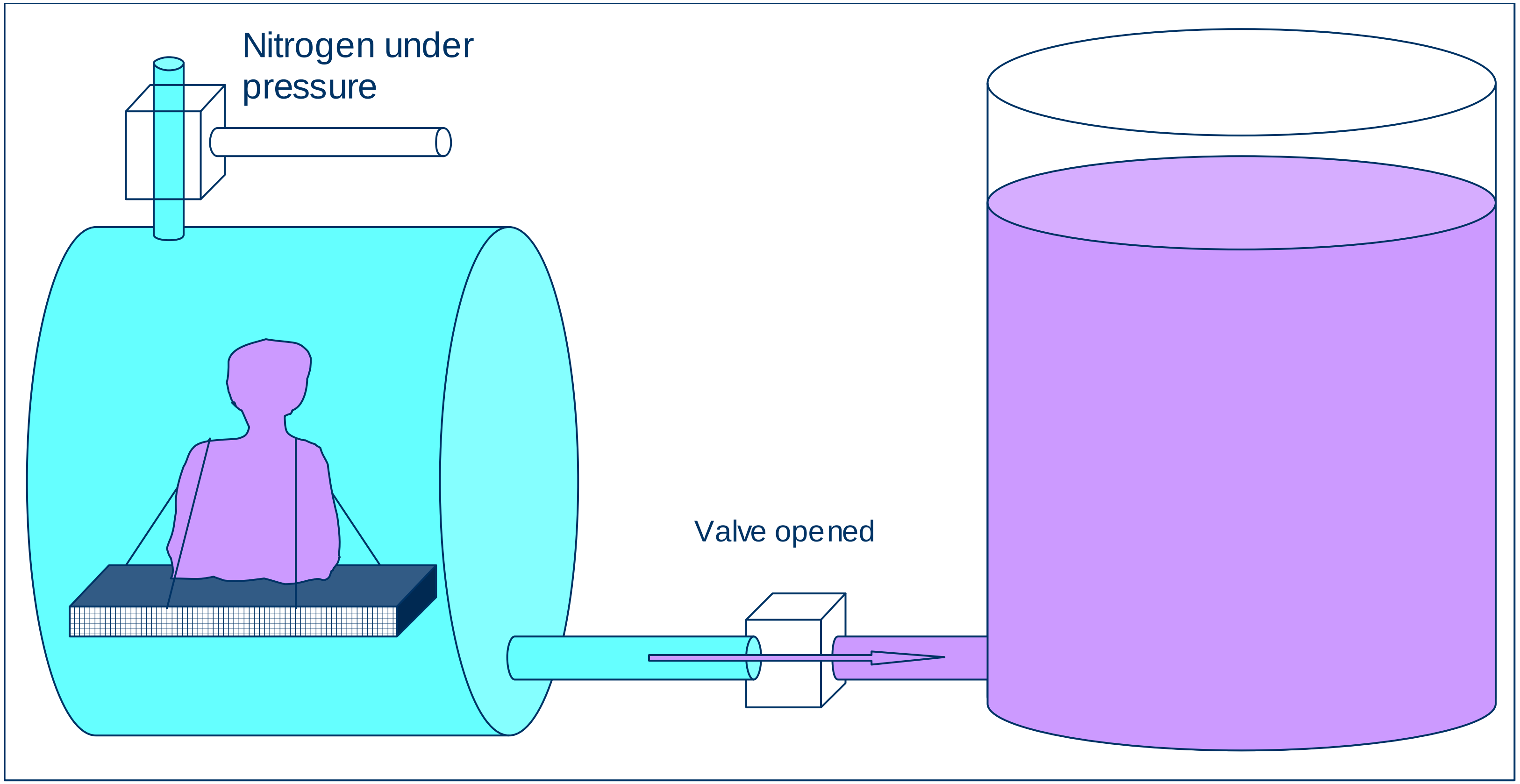
- 3rd step



Diffusion of the resin inside the wood under nitrogen pressure : 2 – 5 bars , 16-24 hours

Impregnation of dry porous material

- 4th step



Emptying of the impregnation tank under nitrogen pressure, then back to atmospheric pressure. The impregnated artefact stays in the tank during some hours for resin draining from the surface of the object

Impregnation tank (vacuum/pressure)   1000 litres

Impregnation tanks   200 litres (left) and 3000 liters

Impregnation of parquet pannels using the 3000 liter tank

Parquet pannels in their support inside the irradiation chamber

Crosslinking of styrene polyester under irradiation

- From liquid to solid

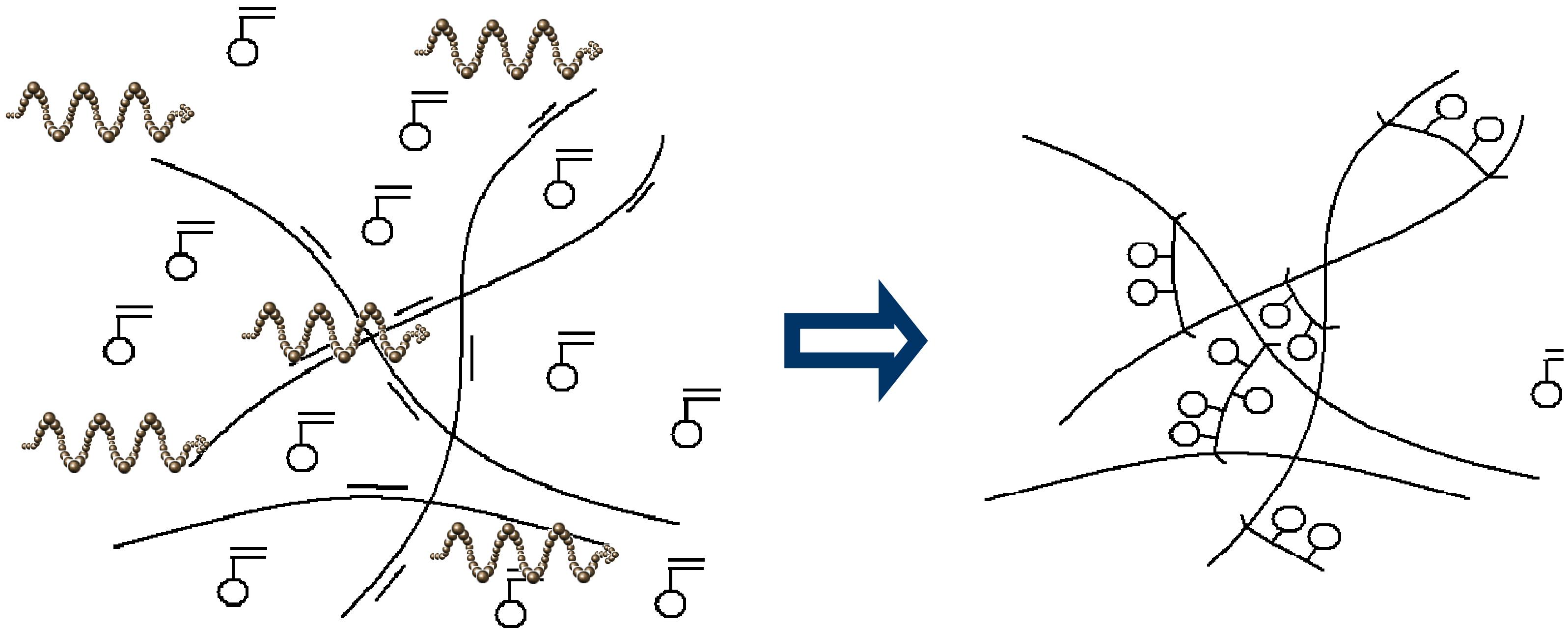
Viscous liquid like olive oil

48% styrene and 52 % mass polyester

Viscosity : 100 centipoises (mPas) at 25℃

Very hard solid

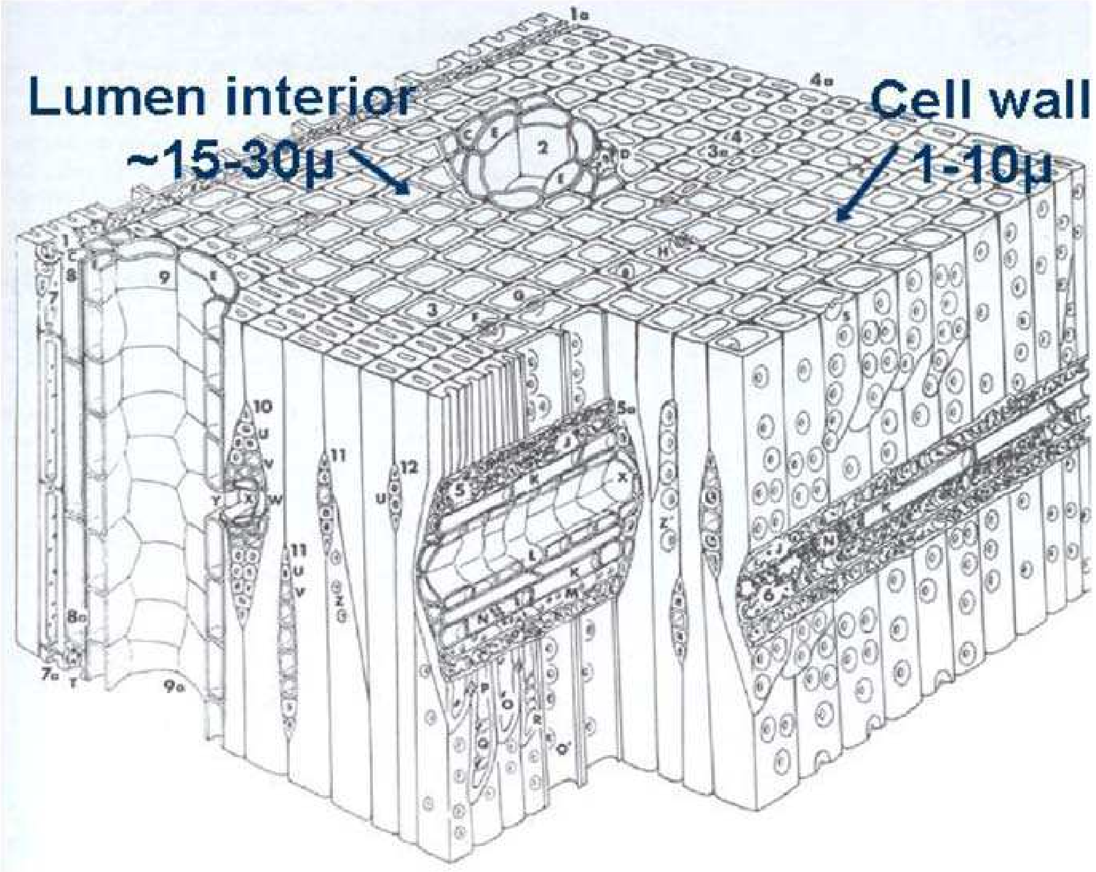
thermoset type like Araldite or epoxy



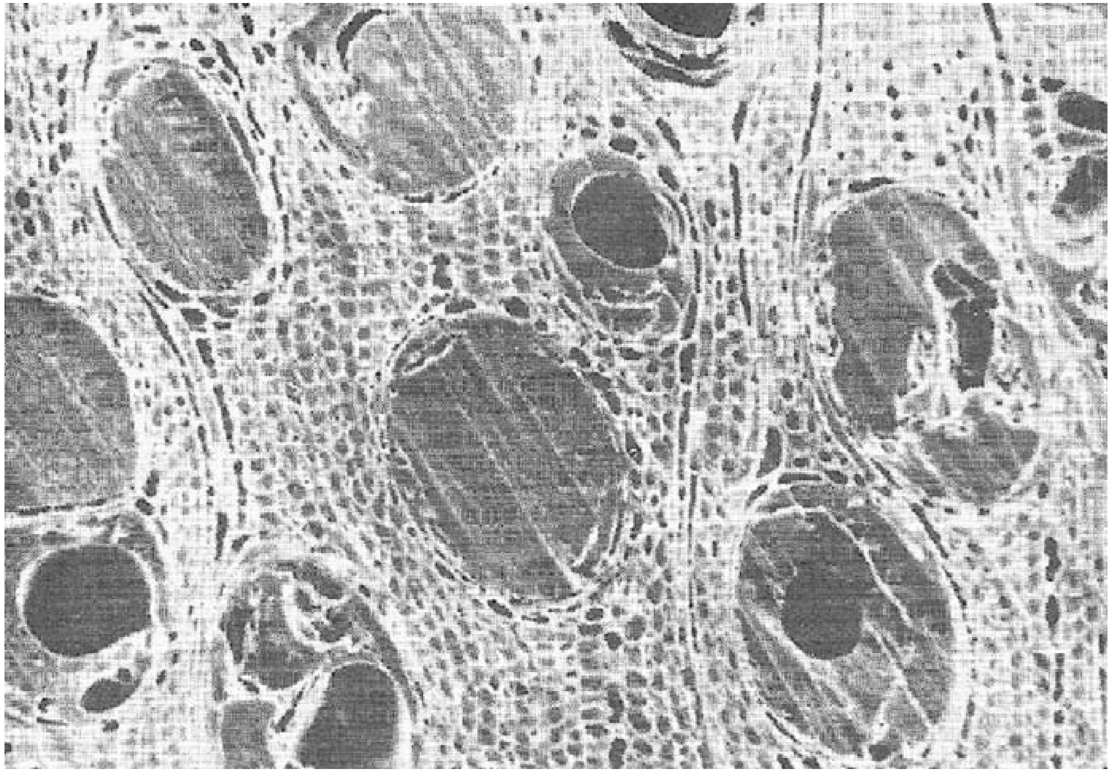
- Crosslinking kinetics controlled by the dose rate (from 0.5 to 1.0 kGy/h), and temperature
- Complete polymerization after ~ 30 to 40 kGy

Parquet pannels after treatment

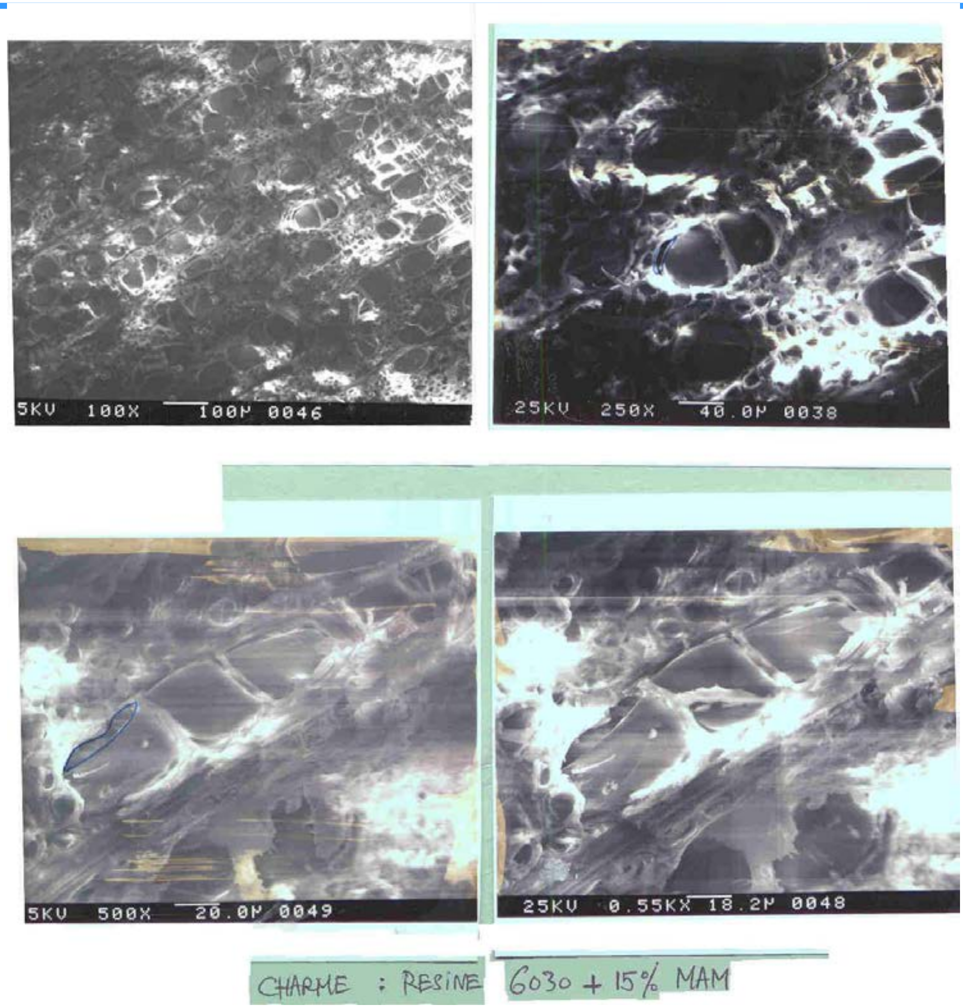
Parquet after reassembling



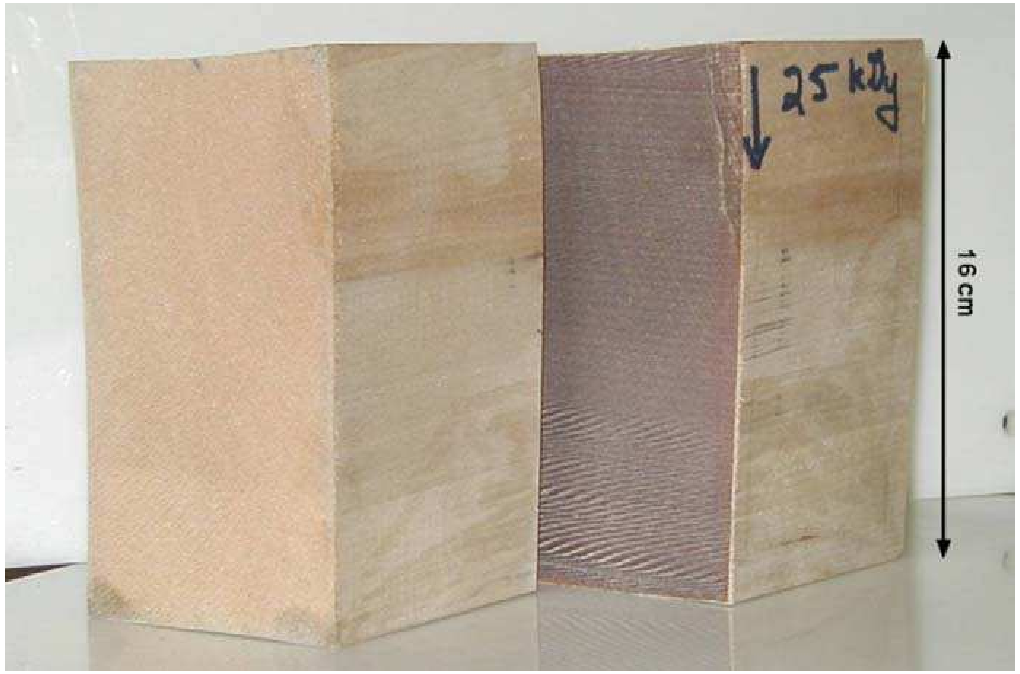
Structure of typical soft wood



Wood impregnated by MMA: incomplete filling of the lumens due to volatilization and monomer shrinkage (20% vol.)
(ref: Rad.Physics and Chem. 78 (2009) 535-538)



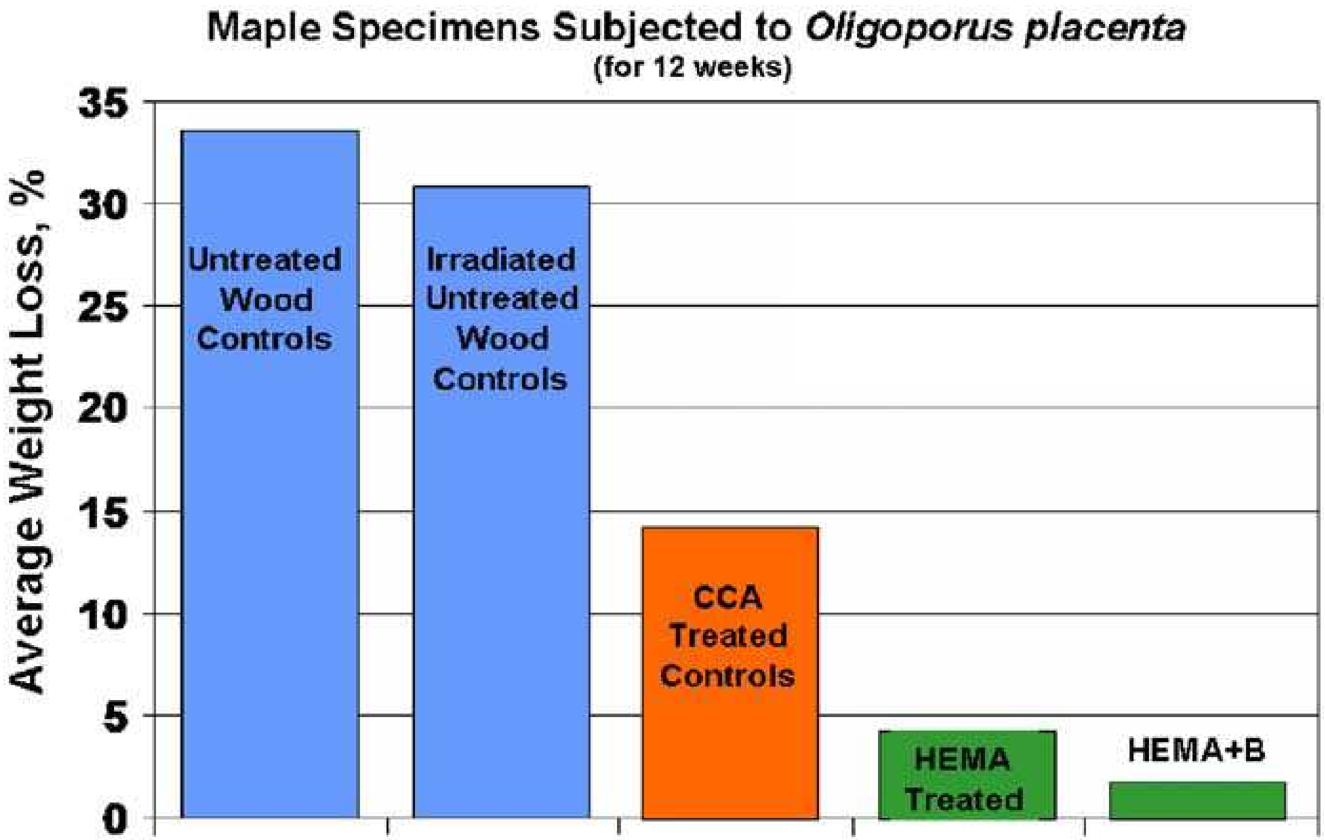
Wood impregnated by polyester resin: complete filling of the lumens, low volatility and low shrinkage (8 %)



Wood impregnated by HEMA: X-ray polymerised impregnant at 25 kGy surface dose
(ref: Rad.Physics and Chem. 78 (2009) 535-538)

Source	EB	X-ray
Maximum energy	5.0 MeV	3.0 MeV
Penetration	1.5 cm	24 cm
Dose rate	6000 kGy/mn	2 kGy/mn (120 kGy/hour)
Dose needed	100 kGy	Less than 25 kGy
Results	Monomer volatility	0.5 % loss
Processing	Multiple pass	Single pass

Wood impregnated by HEMA: X-ray and EB polymerization
(ref: Rad.Physics and Chem. 78 (2009) 535-538)



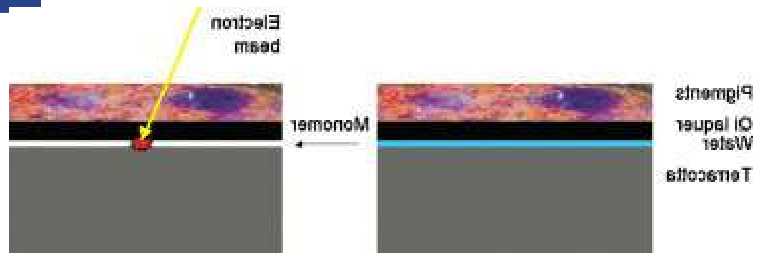
Wood impregnated by HEMA- X ray polymerised at 25 kGy surface dose : Resistance of treated wood to microbial attack
(ref: Rad.Physics and Chem. 78 (2009) 535-538)

Conservation of Chinese Terra Cotta by E-beam curing

Terracotta army of the Chinese emperor Qin Shihuangdi, 91 BC

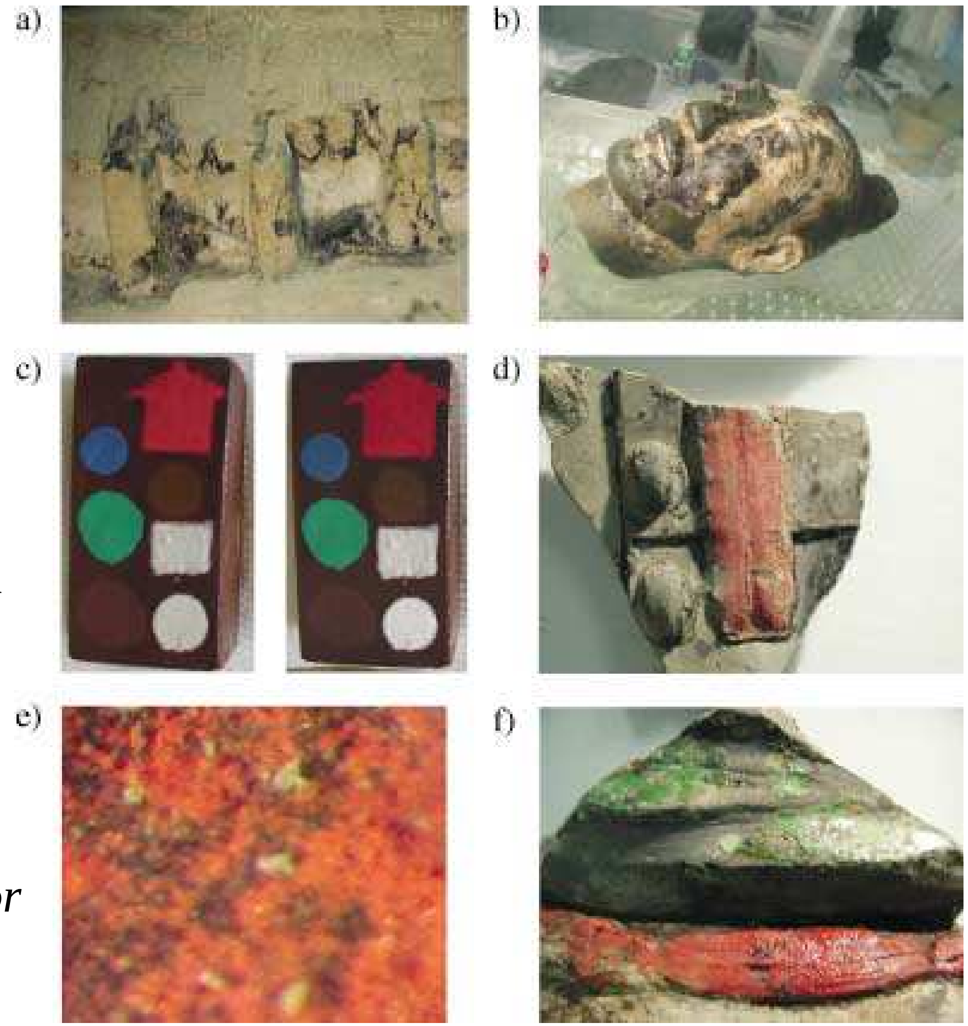
(Ref: *Angew.Chem.Int. Ed*. 2003,42, 5676-5681)

Conservation of the Polychromy of artefacts by E-beam curing



The polymerization takes place mainly in the upper layer of the terracotta, where the electrons are absorbed, and it does not cause any side reactions with the pigments

X-rays and γ-rays either damage the terracotta or do not generate enough radicals.



c) Modern pigments on terracotta. Right: after E-beam irradiation at 50 kGy

d) Fragment from the cuirass of a warrior consolidated by E-beam

Conservation of Chinese Terra Cotta by E-beam curing

Electron Accelerator of Xian Radiation Research Center, Lintong (1 MeV)

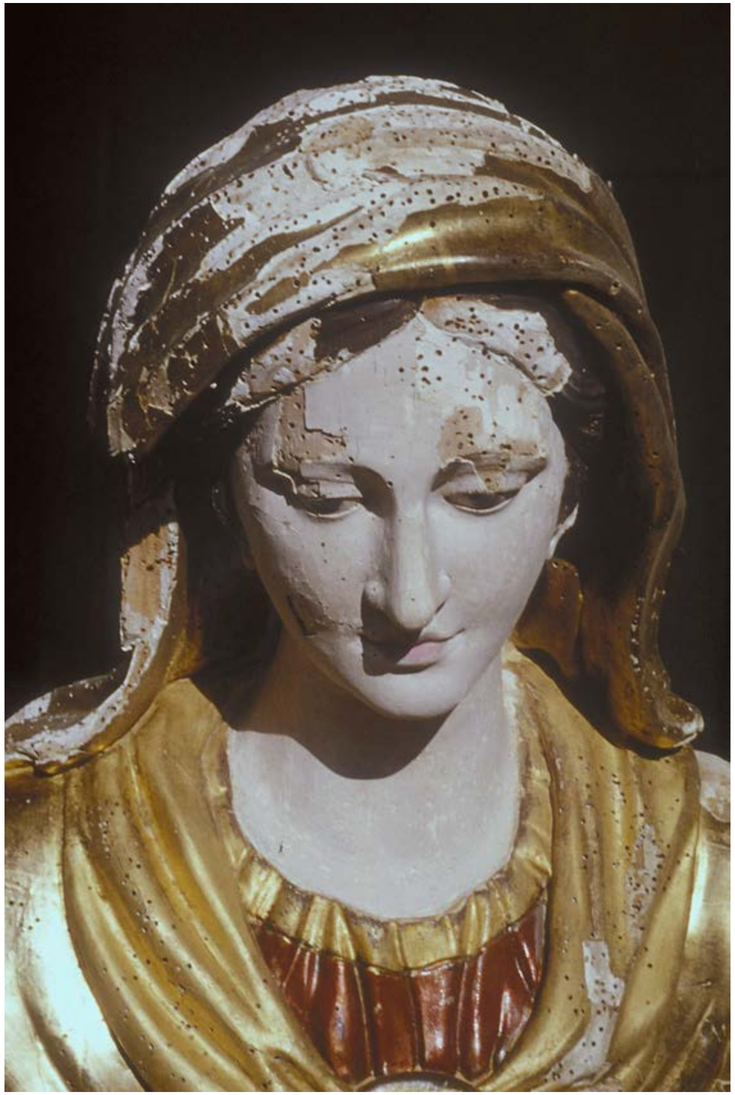
Consolidated artwork, 40 kGy

(Ref: Journal of Polymer Science : part A, vol. 46, 6660-6663, 2008)

Dry porous "Nucléart" consolidation

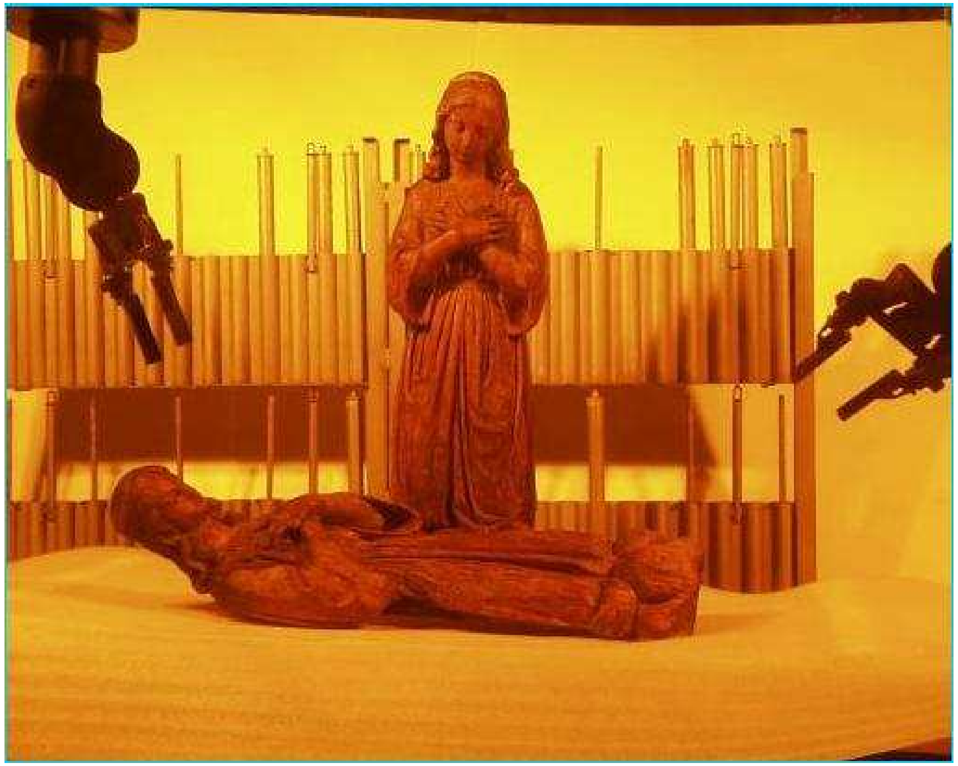
- Historically, the first application for cultural heritage at Grenoble
- A very efficient but irreversible method
- A lot of statues were consolidated during the 70s, 80s and even in the 90s, but it became less employed during the 2000s, surely because curators are more demanding
- in terms of ethics.
- Must be justified:
  - The last chance for very degraded artifacts (polychromed sculpture)
  - When the function of the artifact have to be preserved.

Consolidation of a gilded sculpture



Consolidation of a gilded sculpture

Gilded sculpture impregnated and wrapped in tissu ready for irradiation



- **Irradiation of the artefact**

- **Cleaning of the wood surface during irradiation for taking off any resin residue on the surface. Temperature control inside the wood during irradiation (less than 60 °C)**

- **Irradiation until complete *in-situ* polymerisation of the resin after 48 hours with a total dose of 30-40 kGy at a dose rate ranging from 0.5 to 1.O kGy/hour**

A typical recent dry wood “Nucléart” treatment

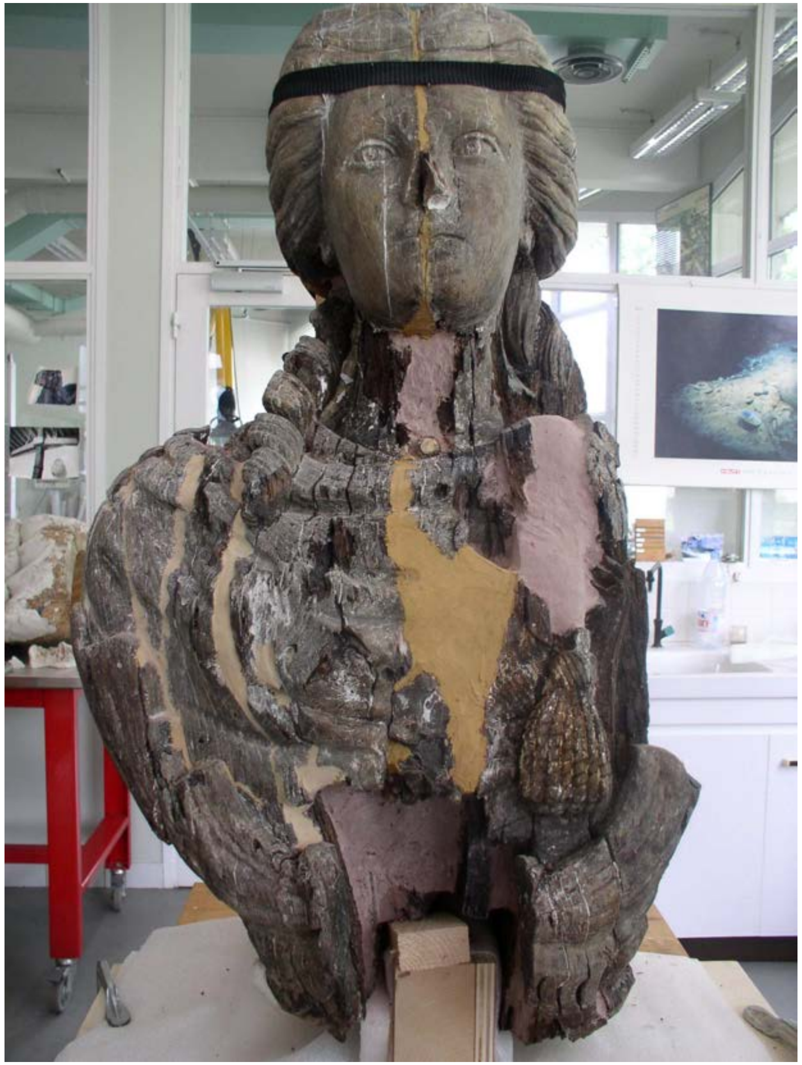
• The « Martha », a figurehead of a schooner of the nineteenth c

A typical recent dry wood "Nucléart" treatment

- Dismantling and « Nucléart » treatment of the different parts

A typical recent dry wood “Nucléart” treatment

- Reassembling after consolidation, and filling the gaps



A typical recent dry wood “Nucléart” treatment

- Final result

St Germain sculpture (XVI th century)

St Germain sculpture (XVI th century)

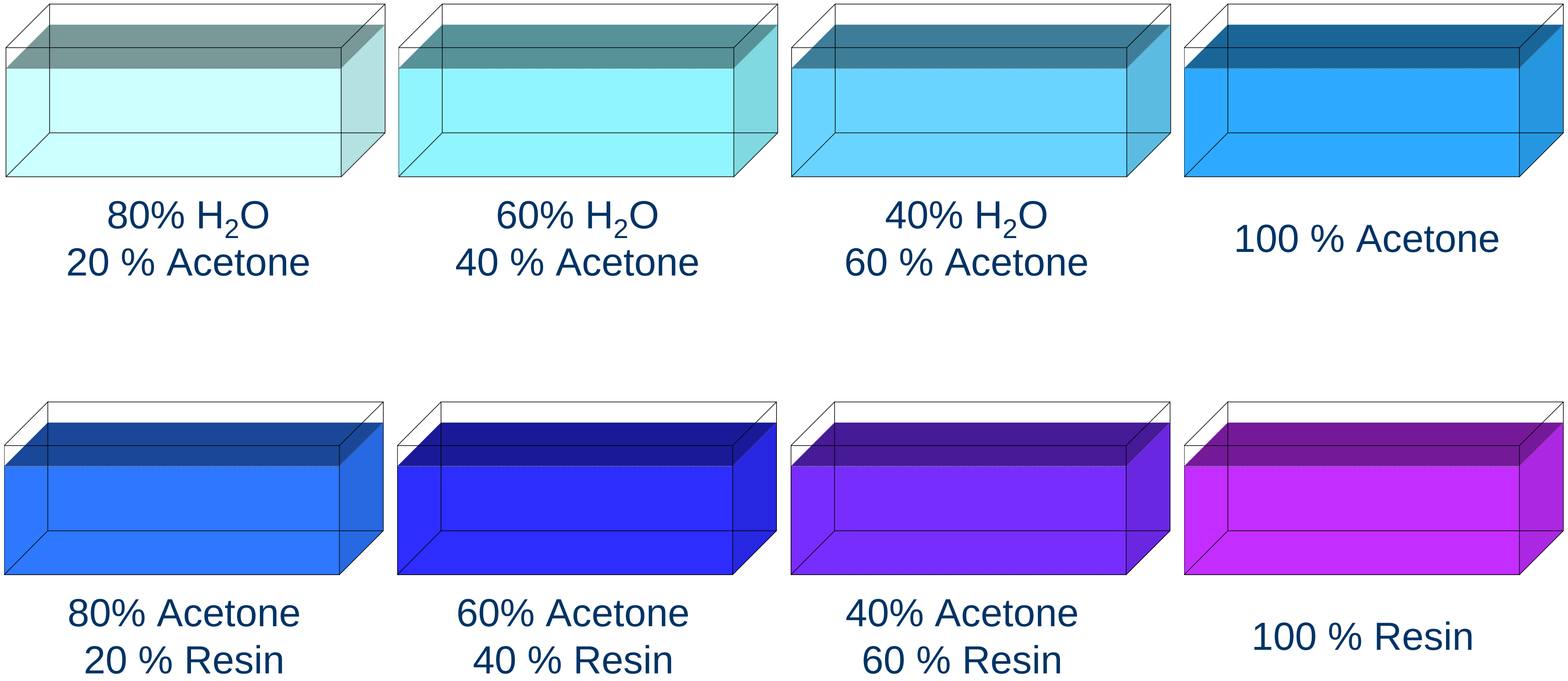
After final restoration

« Nucléart » treatment for waterlogged archaeological wood

- On the archaeological wood, the vacuum pressure impregnation is not possible.
- As the material is already filled with water, it is necessary to replace all the water by the resin, by a complete osmotic exchange.
- But as the resin is not miscible in water, an intermediary solvent must be used, meaning the exchange must be double.
  - water // solvent exchanges
  - followed by solvent // resin exchanges
- The irradiation step is then the same as the one for the dry wood process.

Impregnation of waterlogged wood

- Successive baths, at atmospheric pressure, with different concentrations.



« Nucléart » treatment for waterlogged archeological wood

- A long and complex technique:
  - 1 to 2 years of impregnation,
  - volatile solvent risk,
  - lot of waste,
  - Expensive.
- At the end of impregnation under way, it was agreed to a moratorium, before deciding to work to improve the safety of installations or to replace such treatment by new techniques.
- This method is:
  - still the best in terms of conservation of the initial volume of waterlogged wood,
  - very efficient to avoid corrosion when metal is present near the wood,
  - the only technique to provide encouraging results in the presence of iron sulphide compounds.
- For these reasons, it has became a « best-seller » during the last years, even for more and more massive piece.

A typical recent waterlogged wood "Nucléart" treatment

- « Pierrier du Havre », an antic cannon in metal and wood

A typical recent waterlogged wood "Nucléart" treatment

- Handling after impregnation

A typical recent waterlogged wood “Nucléart” treatment

- Handling in the irradiation cell

A typical recent waterlogged wood "Nucléart" treatment

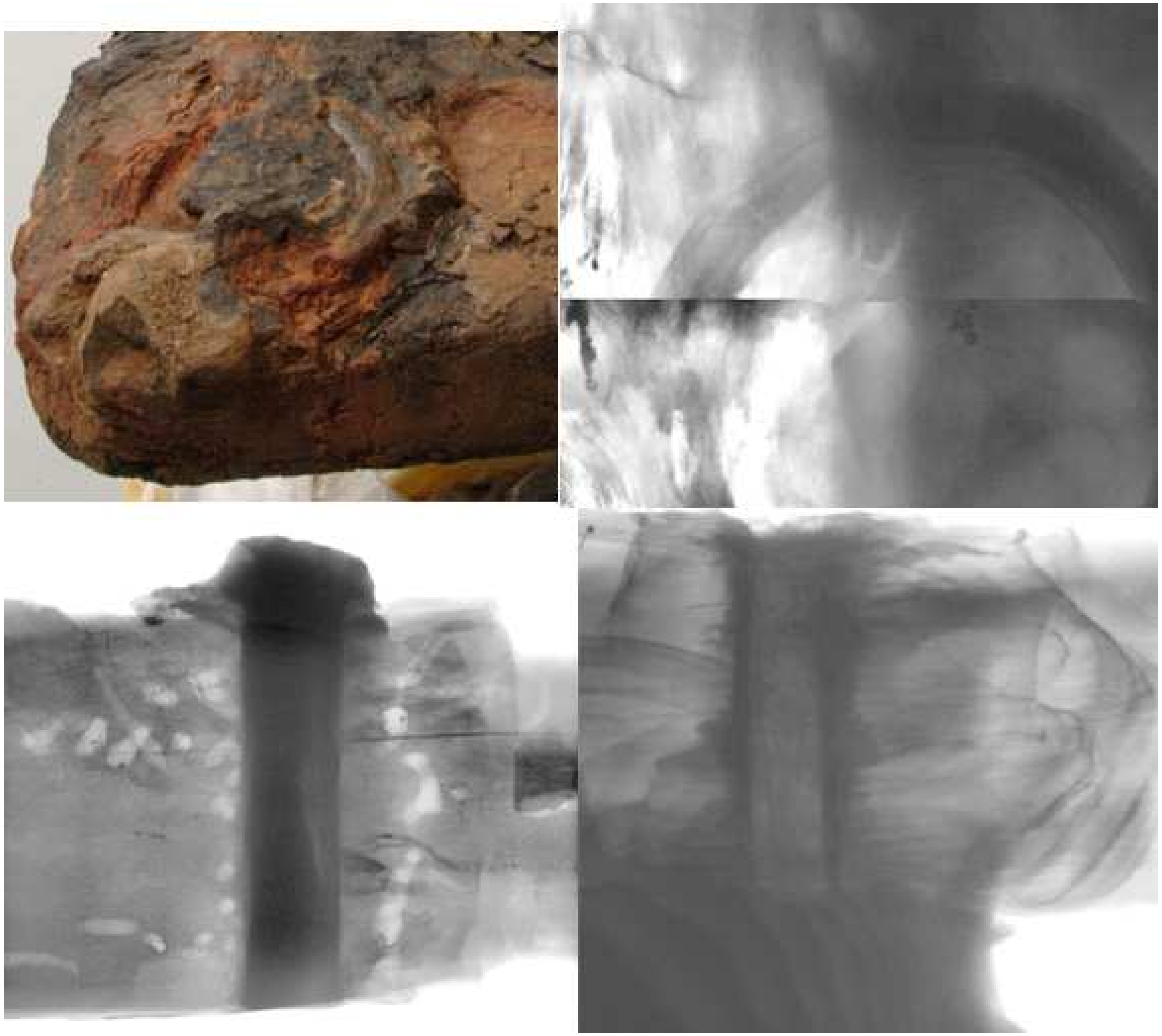
- Removing traces of resin on the surface before the end of the complete polymerization

A typical recent waterlogged wood “Nucléart” treatment

A cannon carriage from a 17th century warship, UK

X-ray radiography of iron inclusions in the wood

X-ray imaging



Transfer in the impregnation tank

Down into the tank

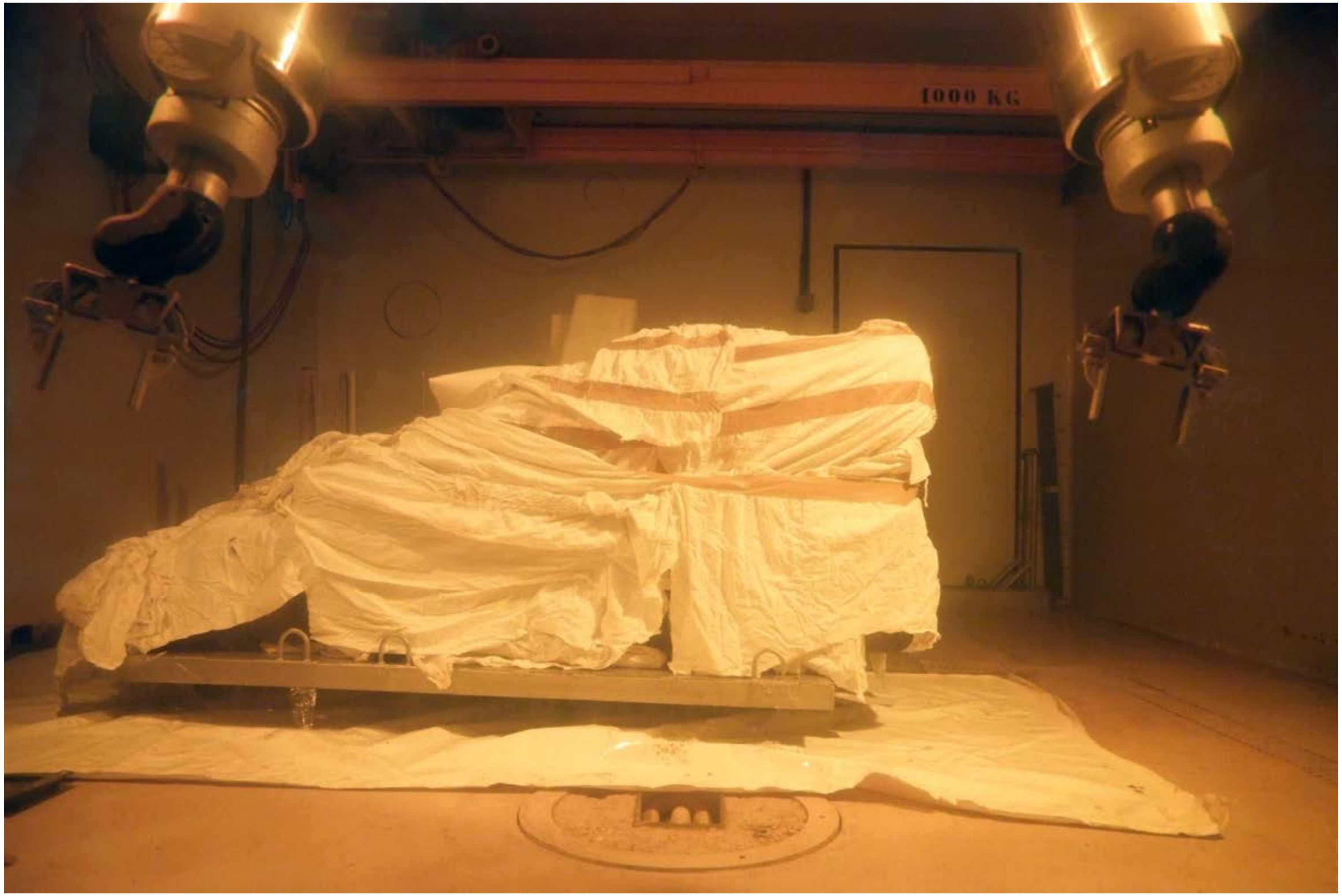
After liquid resin impregnation

Wrapping in textile for absortion of resin on surface

A cannon carriage from a 17th century warship, UK

Wood surface cleaning during irradiation phase

A cannon carriage from a 17th century warship, UK



Carriage in the irradiation chamber

A cannon carriage from a 17th century warship, UK

Carriage without tissue in the irradiation chamber

A cannon carriage from a 17th century warship, UK

After treatment December 2009

A cannon carriage from a 17th century warship, UK

The CEA-Grenoble team (Characterization & Preservation) behind the conserved artefact

Know-how transfer ? Yes, we can !

Mexico 2006

Hvala vam na pozornosti !