INTERNATIONAL ACADEMY OF WOOD SCIENCE • IAWS •

IAWS Academy Lecture

Xavier DEGLISE

IUFRO Division 5 Conference

Xavier Deglise

Professor Emeritus
Honorary Director and Founder of ENSTIB (School of Wood Science and Timber engineering)
Former Director and Founder of LERMaB (Joint research Unit on Wood Material)

A Scientific Itinerary:
Physical Chemistry to Wood Science

LERMaB (UMR INRA n°1093)
Faculty of Sciences and Technologies
B.P.239, 54506 Vandoeuvre les Nancy Cedex, France

Links with Taiwan

Start in 1988 with the PhD Thesis (88-91) of Dr TSOU (TFRI), prepared in Nancy

Pizzi

Tsou

Tomita

Hse

XD

J.C.Yang, Dir.

IUFRO Div 5 Nancy 1992

1996 Shang-Tzen CHANG
Visiting Professor Nancy

ICEUPT 99

Agreement INRA /Taiwanese Ministry of Agriculture

- 2001 Invitation XD TFRI
- 2002 Invitation P.Triboulot TFRI

2005 Visit of Dr.RAO Yu-Chen
Department of Standards
Ministry of Economic Affairs

2006 Dr. TSOU Prof. Toko University
Visiting Prof. Nancy Univ.

Not only the famous frigates!

Personal Itinerary

1958-1960
Paris
Same college:
Molière, Voltaire
V.Hugo, Chirac !

Carte de France - French map

1968 -1970
Quebec, Canada
Ass. Prof.
Phys. Chem.

1961-1968
Nancy
M.S.ChemEng.
PhD, Dr.Sc.
Phys.Chem.
(Photochemistry

Nancy/Epinal
1970 – 1980
Phys.Chem
1980 – 2005
Wood Science

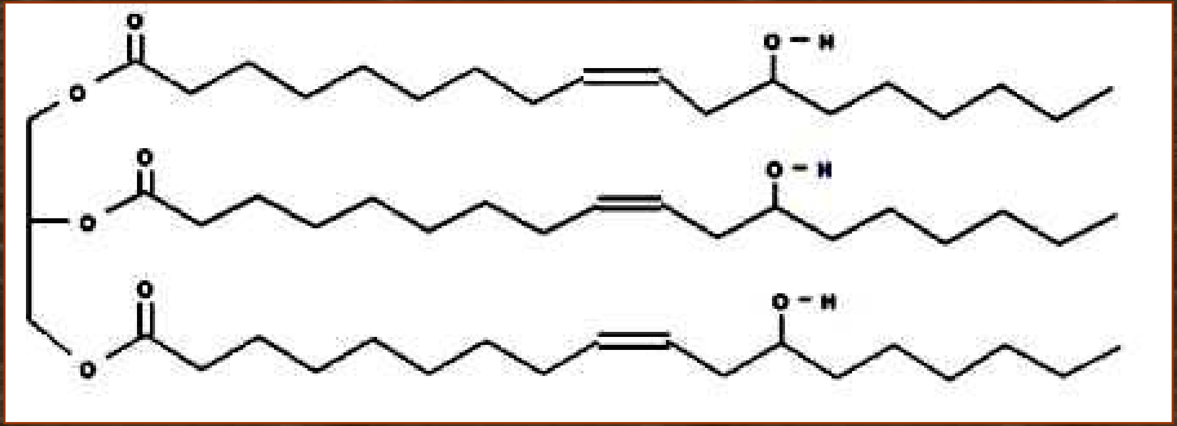
1941,Born in Toulo
Father in the Navy

Scientific background
1964 - 1978

Background in Chemical Engineering

- Marseille 1964, ½ Year as Process Engineer in a Plant producing Rilsan®. This plant belongs now to ARKEMA

- Rilsan as Polyamide 11 is a sustainable polymer, the only polyamide derived from castor oil plant-based renewable resources: Ricinoleic acid



- I was in charge of the dimensioning of a new energy (steam) circuit in the Plant

- Interest for Wood: Design of Gasifiers

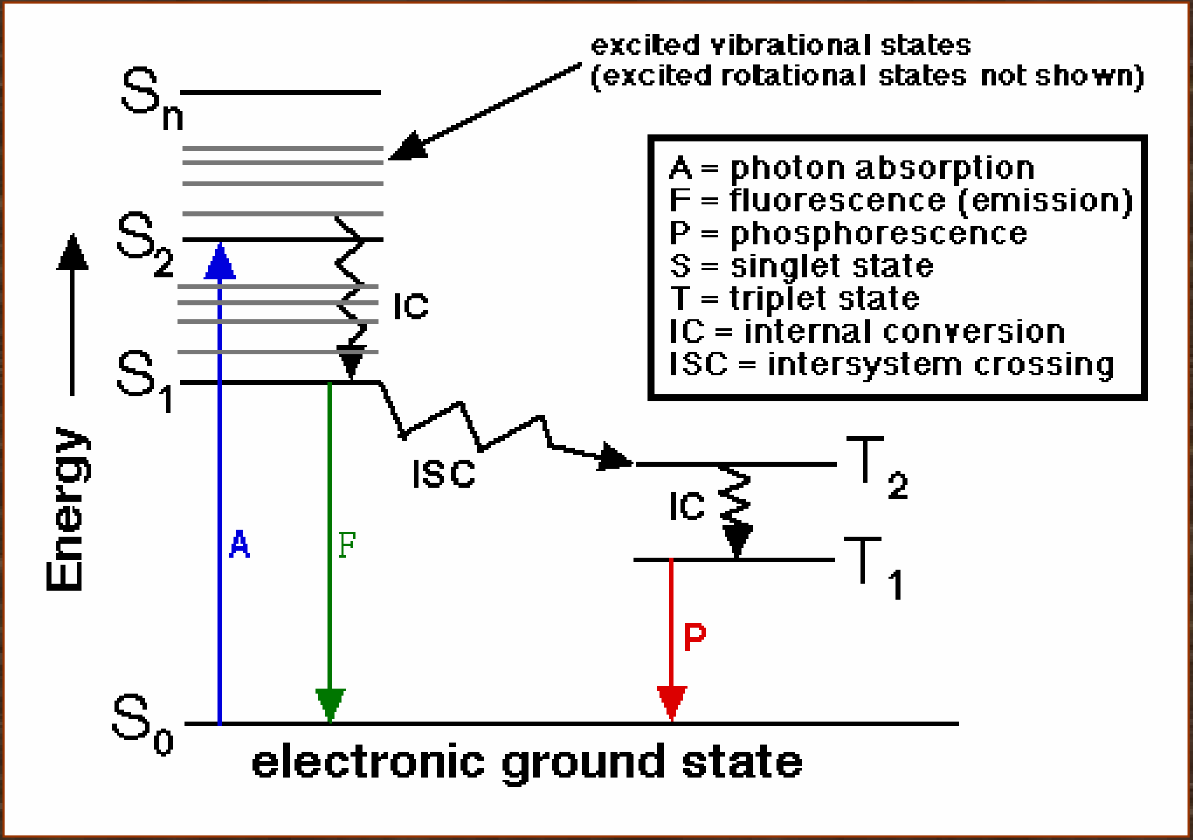
Background in Physical Chemistry

- Nancy 1964 – 1968 : Photochemistry – Photo physics

- Preparation of Doctorate Thesis on Photo oxidation, with Jacques Lemaire:

- actually specialist (emeritus) on Photo-protection of plastics, polymers, organic coatings.

Modeling of Electronic Energy Transfer between Excited States, Triplet states (T_1, T_2) and Singlet States (S_1, S_2, …S_n) of different molecules within molecular distances. (Theoretical Chemistry)



Interest for Wood:
- Absorption of Solar Light
- primary steps of wood photo-discoloration
- UV stabilizers for wood and coatings

- Photoxidation of E-isomer of (*E*)-2-Butenal (crotonaldehyde)
$CH_3CH{=}CHCHO$ (RCHO)

$RCHO\ (S_0) + h\nu \longrightarrow RCHO\ (S_1) \longrightarrow RCO. + H.$

$H. + RCHO \longrightarrow RCO + H_2$

$RCO. + O_2 \longrightarrow RCO_3.$

$RCO_3. + \underline{RCHO} \longrightarrow \underline{RCO_3H} + RCO.$

Inhibition of the reaction by adding antioxidants

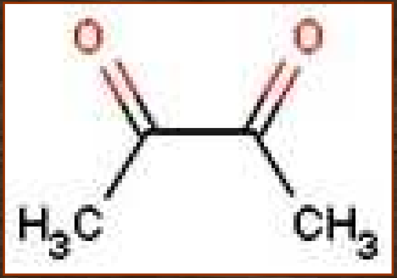
$RCO. + RCO. \longrightarrow RCO. + RCO.$

. . . .

IR spectroscopy was used to analyze the products and O_2 consumption for the kinetics, and mechanism of reaction

Interest for Wood: Prevent oxidation of wood, role of phenol extractives, determinism of wood color stabilization and protection. Stabilization of coatings

- “Determination” of the T_2 of 2,3-butanedione or diacetyl which is a vicinal diketone.



By photolysis, a conjugated Enol was formed after absorption and intersystem-crossing to the second triplet state:

$$CH2 = COH - \overset{\overset{\large O}{\|}}{C} - CH3$$

UV spectrometric determination of enol gives the energy of the T_2

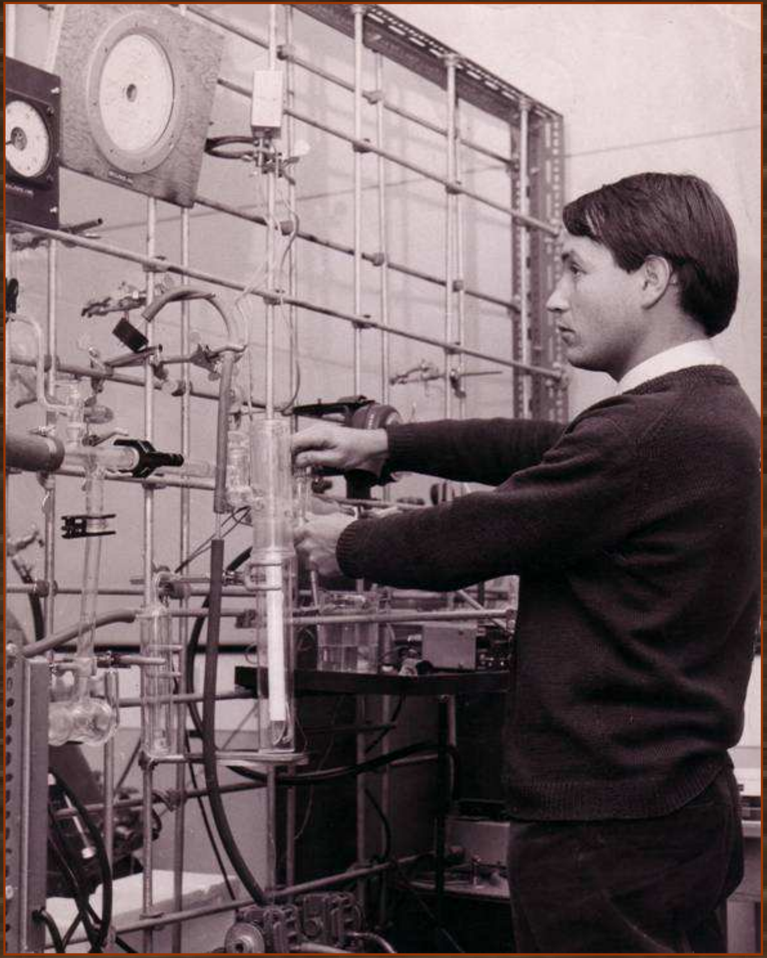
Interest for Wood: UV spectrophotometer is a powerful tool for the determination of absorbance spectra and color measurements. Same for the energy of excited states of molecules

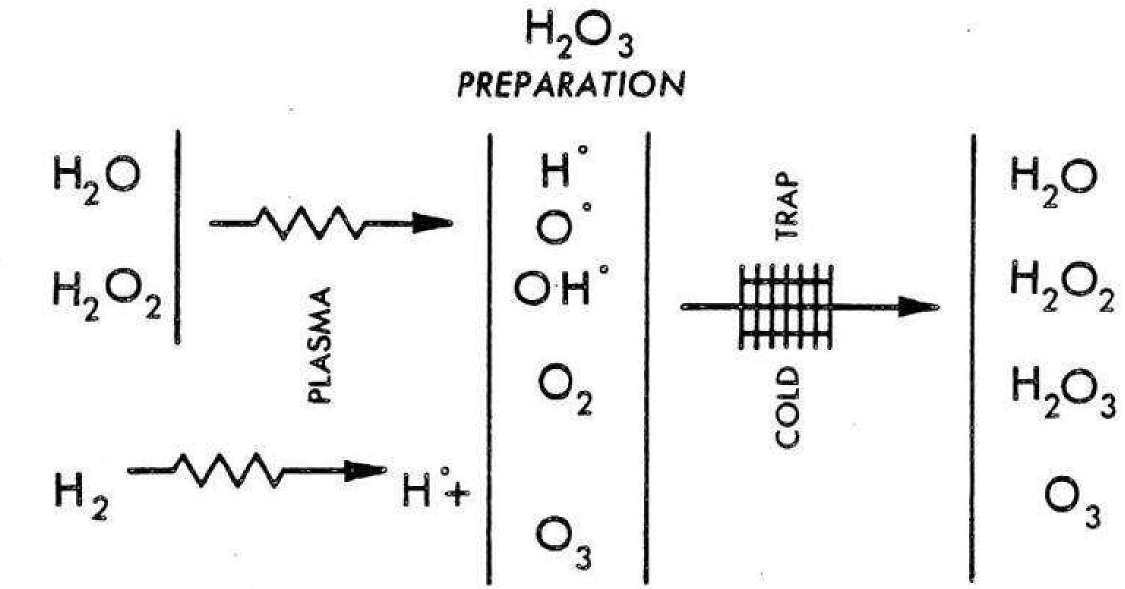
Laval University, 1968 – 1970, Quebec, Canada

Poly-oxides team
P.A. Giguère

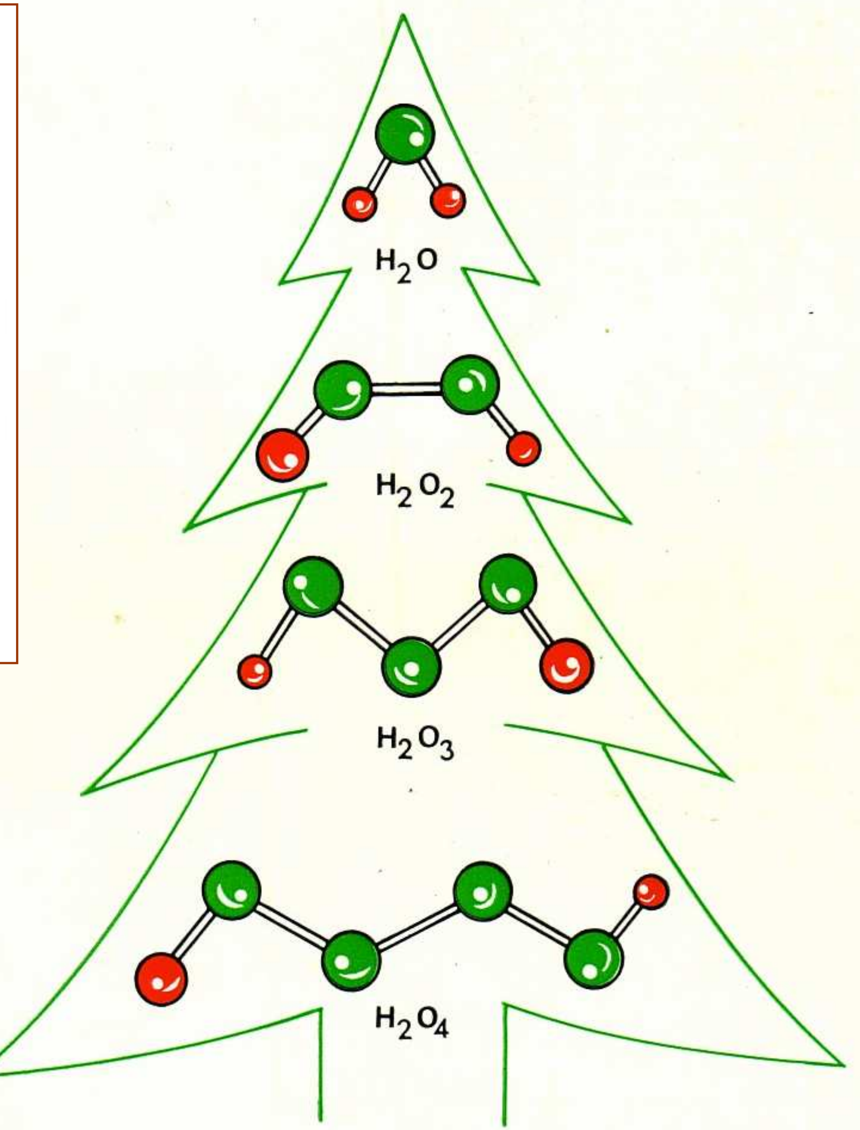
My best period as Scientist!
Enthusiasm, Risk, Challenge…

"Discovery" of transients poly-oxides: H_2O_3 and H_2O_4 . Lifetime: seconds at room temperature, hours at 50°K





Reactions involved in preparation and stabilization of H_2O_3 molecules



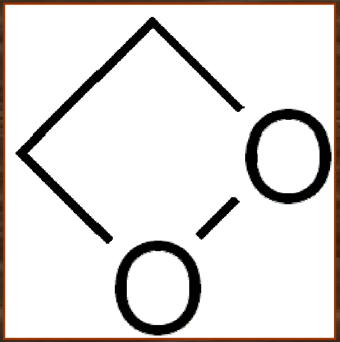
Cold Plasma with Microwave or RF Generator
Low temperature matrix isolation (Liquid N_2)
IR and Laser Raman Spectroscopies
Double isotope effect

Interest for Wood: Plasma and Corona treatments of Wood surfaces and coatings to increase adhesion (gluing, finishing, wood modification)
IR and Raman Spectroscopies to analyze the chemical structure of wood.

Nancy 1971 – 1978 : Singlet Oxygen, Photo-reactors, Chlorination

- Synthesis of “clean” Singlet Oxygen ($^1O_2\Delta g$) in an Oxygen plasma (Microwave). Normally, it is produced in a photosensitized reaction.

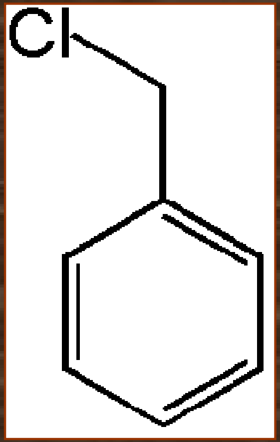
- Reaction of ($^1O_2\Delta g$) with 2,3-dimethyl, 2-butene (H3C-CH=CH-CH3) and of α-Ethylenic Aldehydes. It gives 1,2- dioxetanes substitutes or not.



These dioxetanes are not stable and undergo chemiluminescence with cleavage of the peroxide bond

Interest for Wood: Singlet oxygen is involved in lignin photodegradation

- Photo chlorination of Toluene to give Benzyl Chloride and di or tri chloro substituted Toluene



The mechanism is a chain reaction:

$Cl_2 + h\nu \longrightarrow 2\ Cl.$

$Cl. + \varphi\ CH_3 \longrightarrow \underline{\varphi\ CH_2Cl} + H.$

$H. + Cl_2 \longrightarrow Cl. + \underline{HCl}$

$Cl. + Cl. \longrightarrow Cl_2$

For the design of the photochemical reactor it was necessary to know the light absorption profile inside it.

Interest for Wood: Design of photochemical reactor applied to UV Curing and Coatings photo-degradation

Wood Science. Start in 1978

Why wood research?

- No scientific reason, nor money interest.
- In 70's, Lack of "Wood engineers" in France. "Forest engineers" were involved in Wood Industry, without a good knowledge in Wood Processing.

- In 1978, I start a Professional MS in Wood Engineering, with the support of ENGREF (Forestry School) in Nancy.

This MS was transformed in enstib in 1985

We were supported by **Philippe SEGUIN**, President of Parliament and Ministry of Research and University **François FILLON** who is our actual Prime Minister

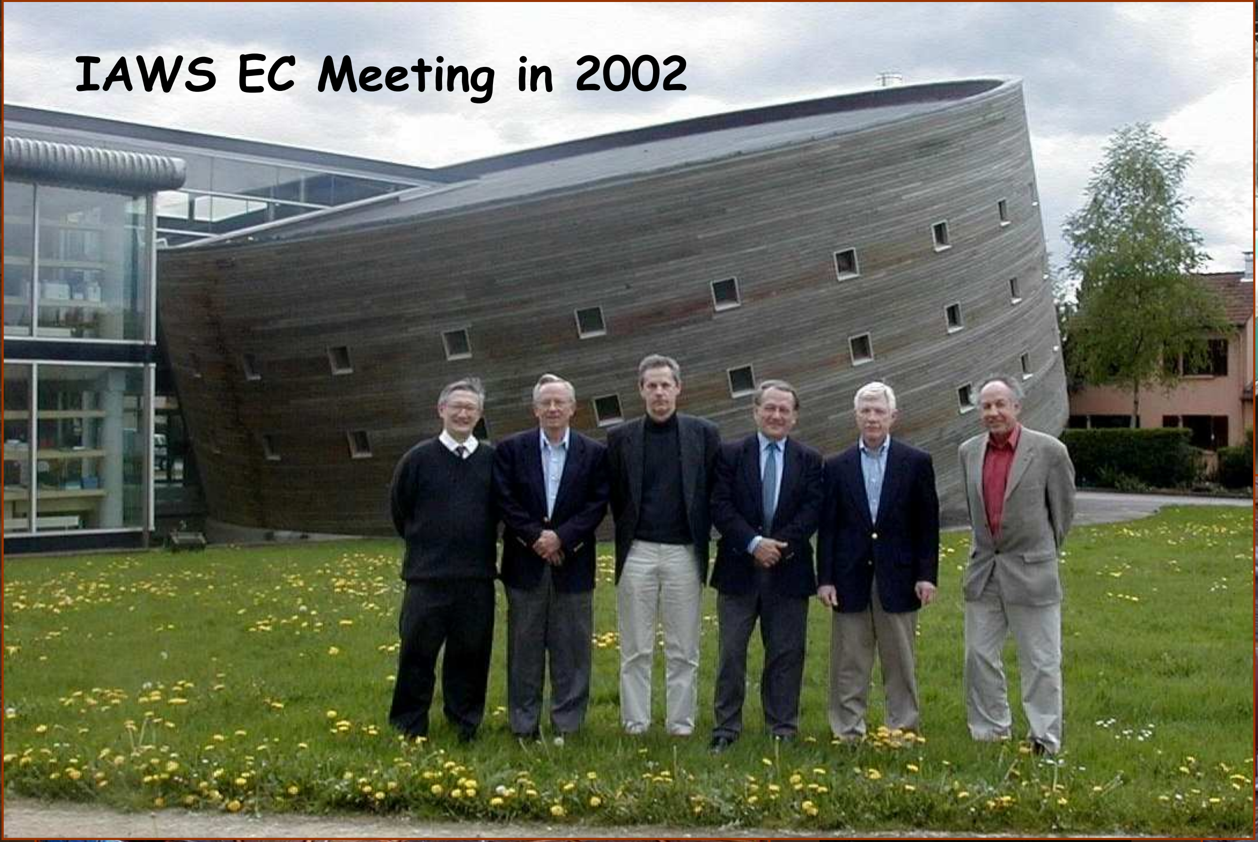
A small team with:

- **Patrick Martin** in Production Engineering
- **Daniel Masson** in applied Chemistry
- **Pascal Triboulot** for the facilities

At start only one had a wood culture! **(P-J. Meausoone)**
Now, the team has 20 Academics, 23 support and administration people

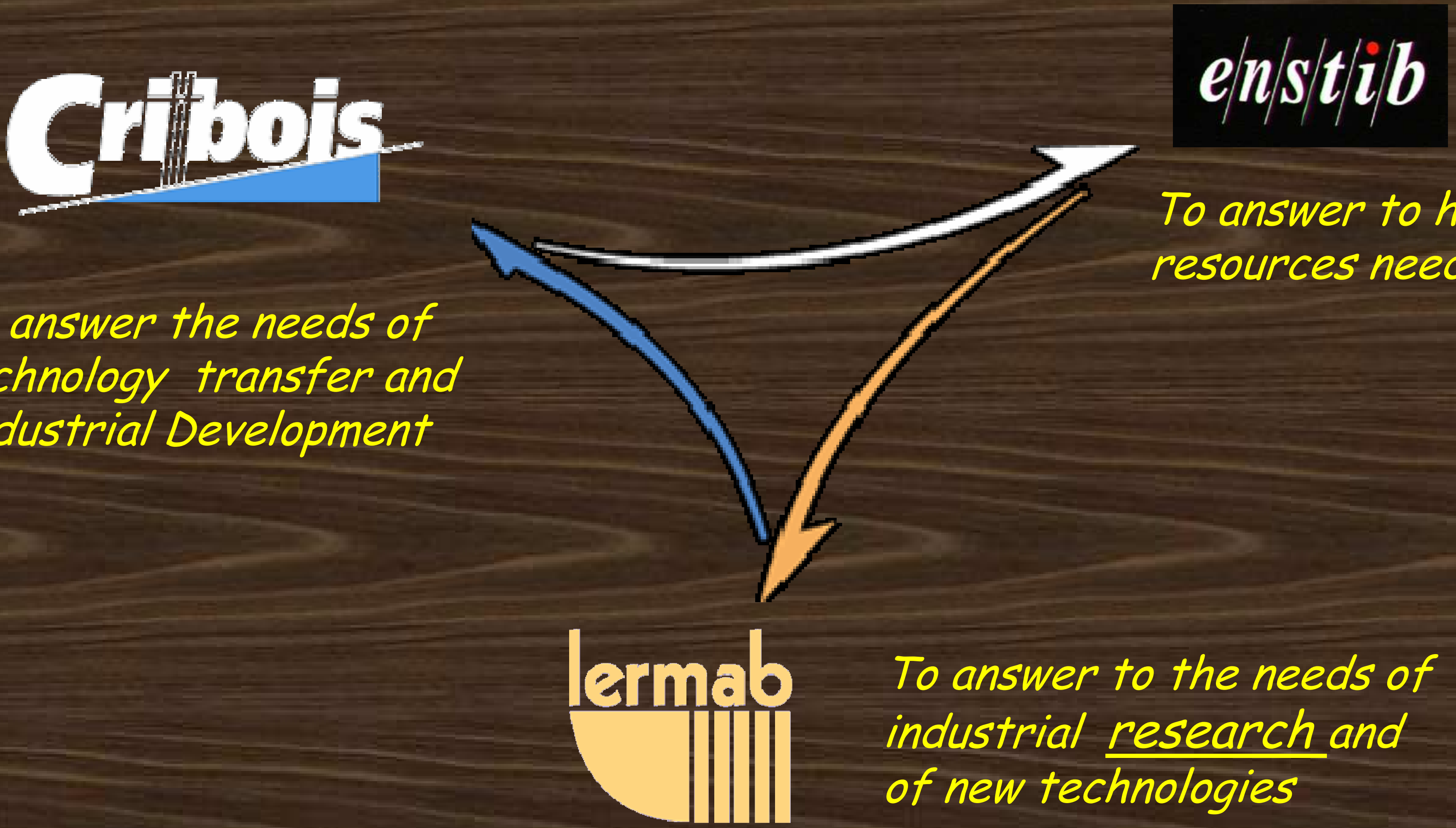
A **Fiber Cluster** (Wood, Pulp and Paper, Textile and Composites) has been created around ENSTIB.

IAWS EC Meeting in 2002



enstib

ENSTIB is an industrial engineer's school. Its core job is to satisfy the needs of Wood industrial sector.

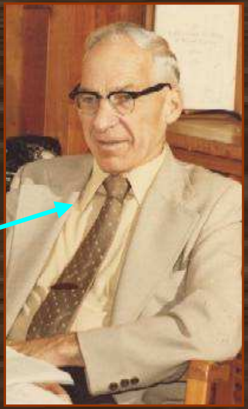


To answer to human resources needs

To answer the needs of technology transfer and Industrial Development

To answer to the needs of industrial research and of new technologies

Research was developed, in the early 80's, thanks to the help and advices of:



- IAWS fellows: Hubert Polge (INRA Nancy), Fred Dickinson (Dir. FPL, UC Berkeley), Robert Youngs (Deputy Dir. FPL Madison), Dr HC Univ Nancy, Walter Kauman (Dir.Sc. CTBA), Dr. Edmone Roffael (WKI)
- Sabri Ergun (SRI….and equation!), Pierre Bouvarel (INRA - ENGREF)
- German scientists with my first visits (1977) of German facilities BFH in Hamburg, WKI (Fraunhofer Institut für Holzforschung) in Braunschweig, Holzforschung in Technische Universität München

4 Research Teams have been formed:

1. Wood Machining and CAD / CAM, Prof. P. MARTIN
2. Process Engineering, Prof. A. ZOULALIAN (LERMaB)
3. Organic Chemistry and Microbiology, Prof. B. LOUBINOUX (LERMaB)
4. Physical Chemistry and Polymers, XD (LERMaB)

In 1993 the three last teams joined in LERMaB

In 1999, the ENGREF Team "Wood Anatomy and Physics", headed by P.PERRE, joined LERMaB….which was "upgraded" in 2000 as INRA Joint research Unit.

Wood Physical Chemistry ?

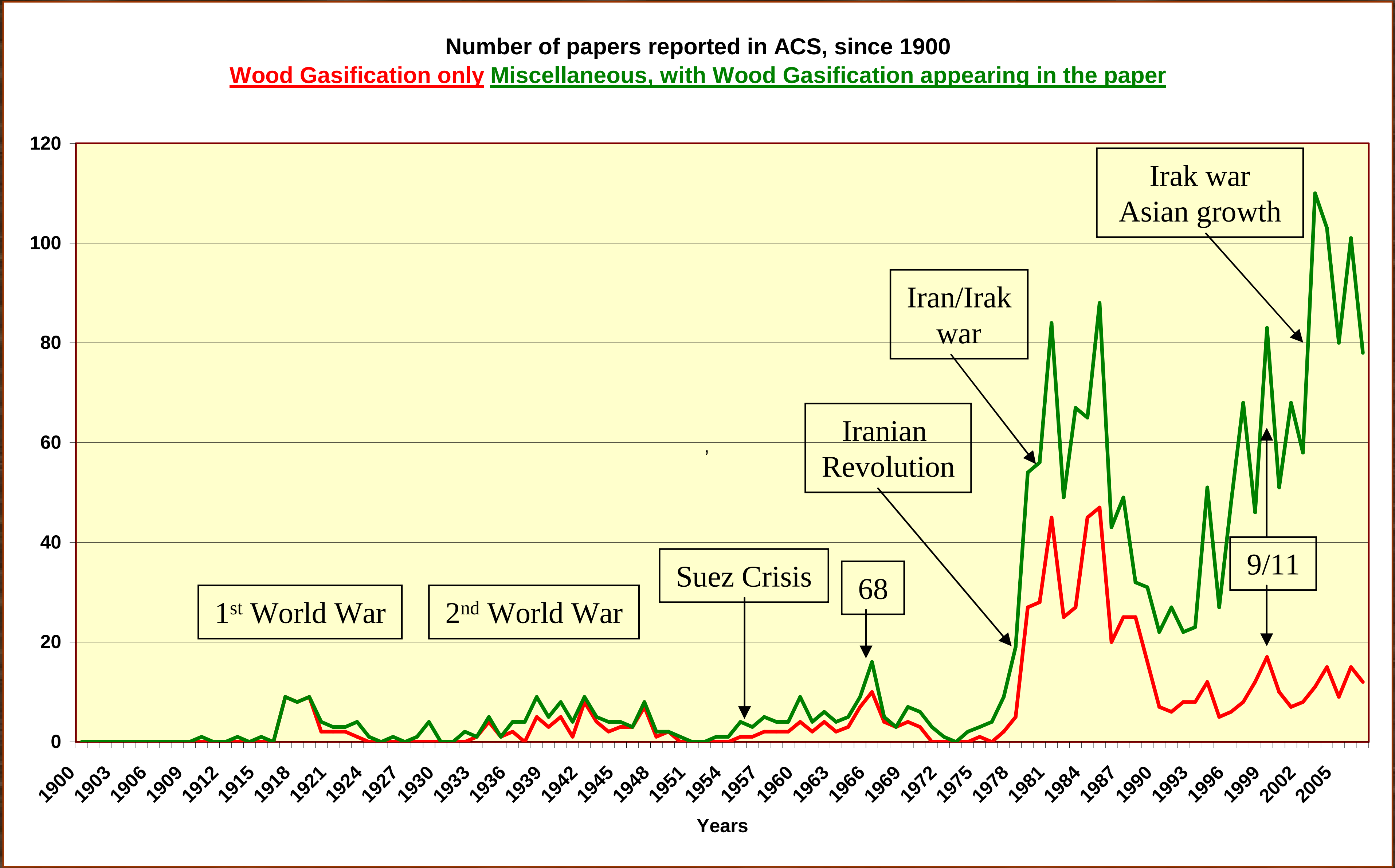
Start in **Wood Energy**, as we had a Background in Kinetics of Hydrocarbons Pyrolysis and in Chemical Engineering.

Besides, to start, a complete Wood knowledge was not compulsory !

And it was the best time! **Oil crisis (80)!**

Gasification by Fast Pyrolysis with **Pierre Magne**
Direct Liquefaction with **Daniel Masson**

Thermal Process	Temperature	Atmosphere	Products
Combustion	> 900°C	O_2 (air)	$CO_2 + H_2O + N_2$ + ashes to be treated
Pyrolysis	< 700°C	Inert gas or Low pressure	char + tars + gas, which proportions are related to the pyrolysis parameters
Gasification by Fast pyrolysis	> 700°C	Inert gas or Low pressure	Mainly gas (CO, H_2, CH_4, C_2H_4 …) with low quantity of char used
Gasification	> 800°C	Air or H_2O vapour	Gas (H_2, CO, CO_2, CH_4, N_2) + ashes to be treated
Liquefaction by Fast Pyrolysis	< 550°C	Low pressure	High viscosity liquid (phenols)
Direct Liquefaction	300°C- 350°C Slurry in water	CO High pressure	High viscosity liquid (phenols) non soluble in water

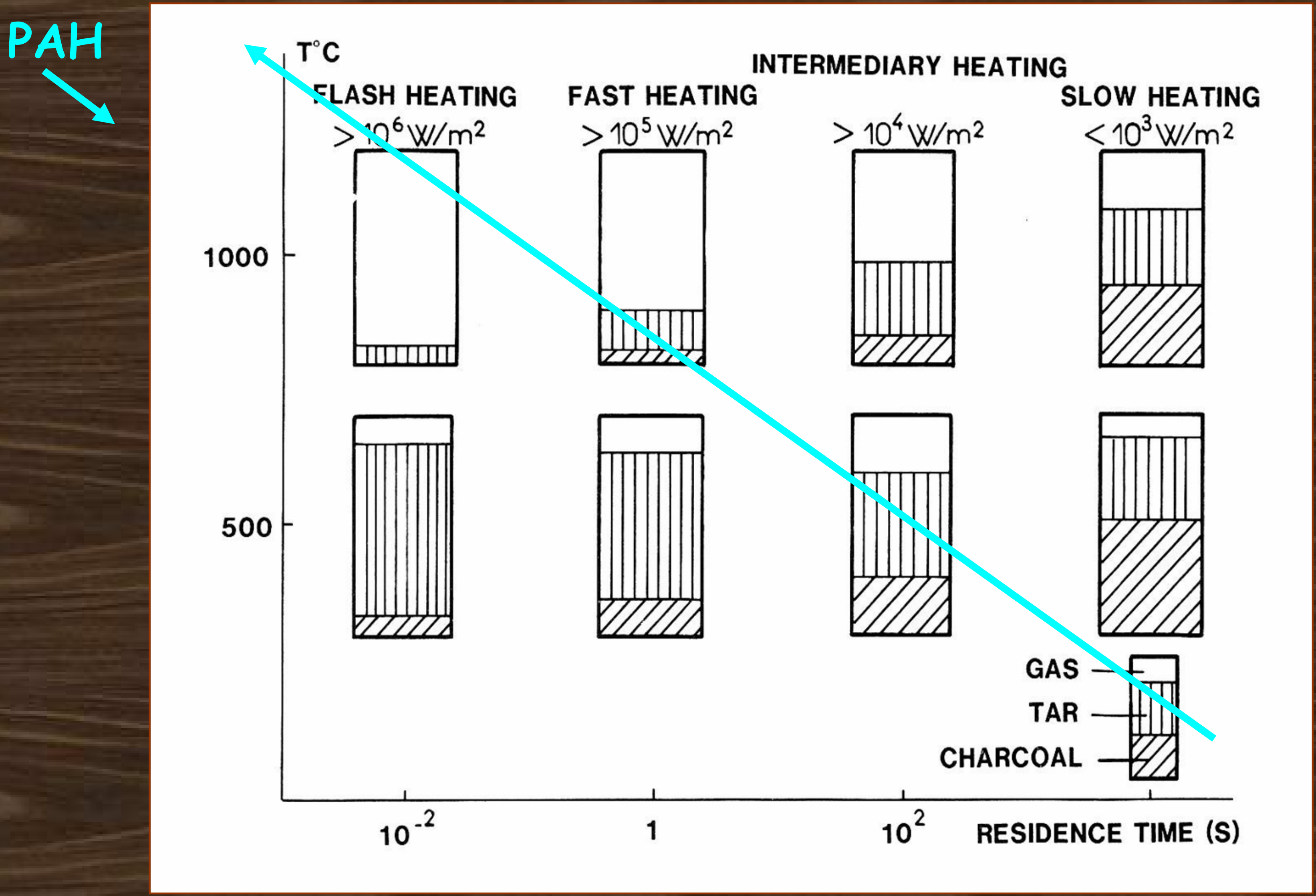


Number of papers reported in ACS, since 1900

Wood Gasification only Miscellaneous, with Wood Gasification appearing in the paper

Gasification by fast Pyrolysis

Basic research in kinetics show us that pyrolysis was a flexible reaction



“Solar Gasification” and Catalytic Fast Pyrolysis

In 1980, project on solar gasification complete at high temperature > 1000°C was funded by CNRS CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

To achieve a complete gasificati without tars, we have studied catalytic pyrolysis at high temperature (Claude Richard) → with carbonates, phosphates, chlorides of Na, K, Ca, Zn, Ni.

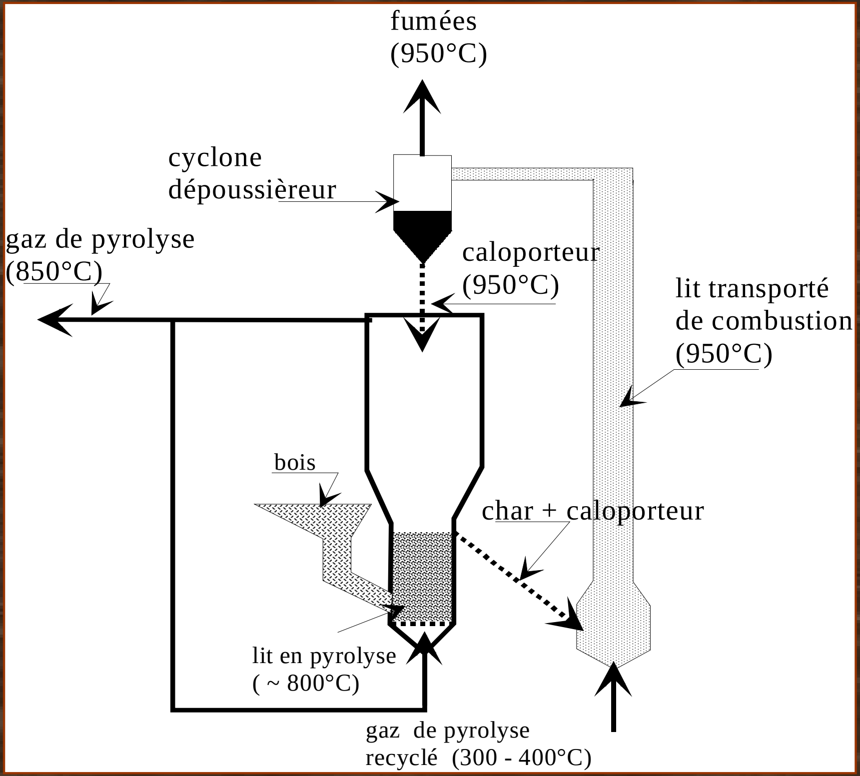
Chemistry was successful, Economy?

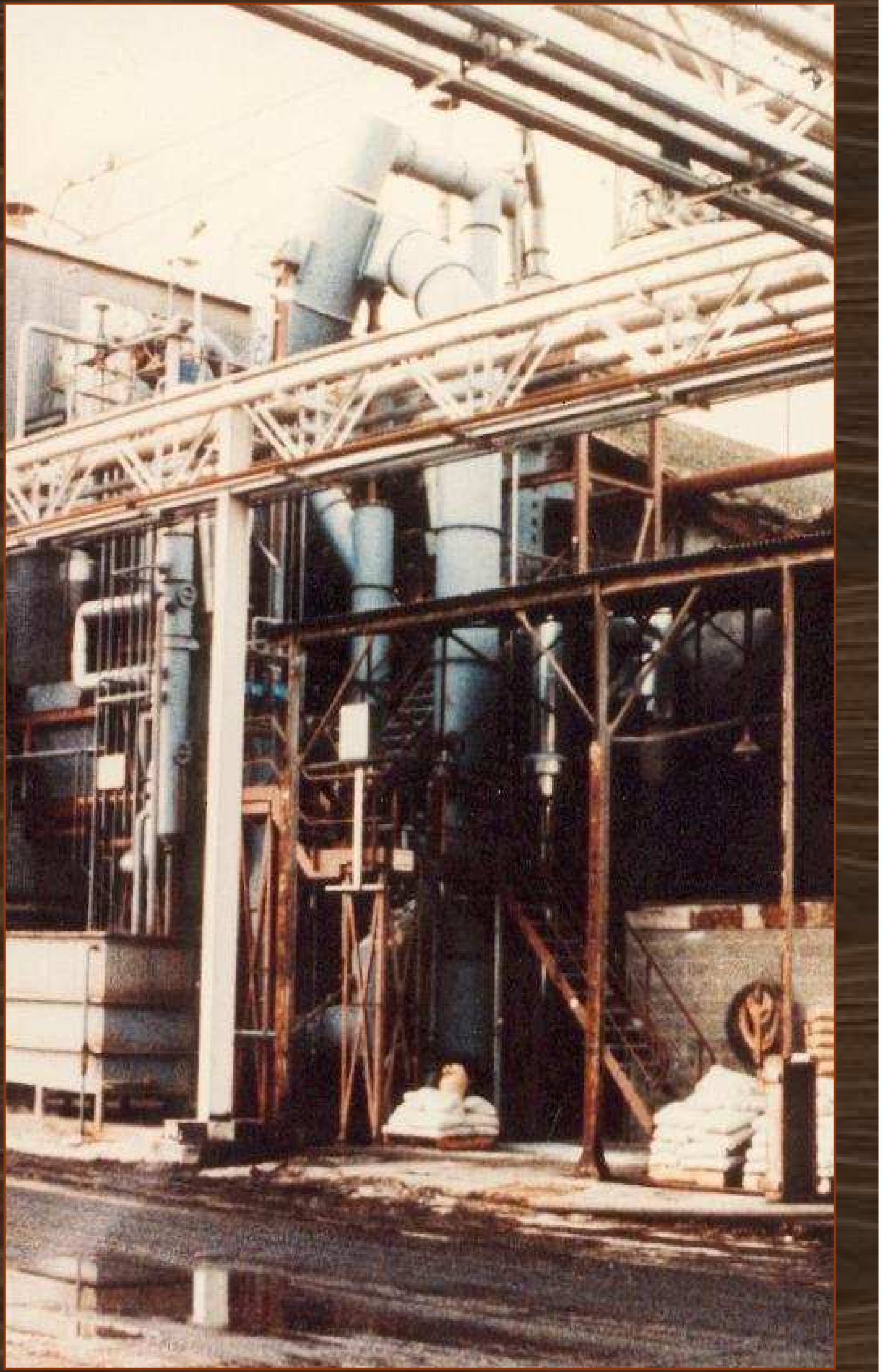
Development of Pilot scale CFB for wood gasification by fast pyrolysis with Saint Gobain Cy (1984/1986).

Capacity 500Kg/H-1T/H pine barks. Power ~ 2 MW

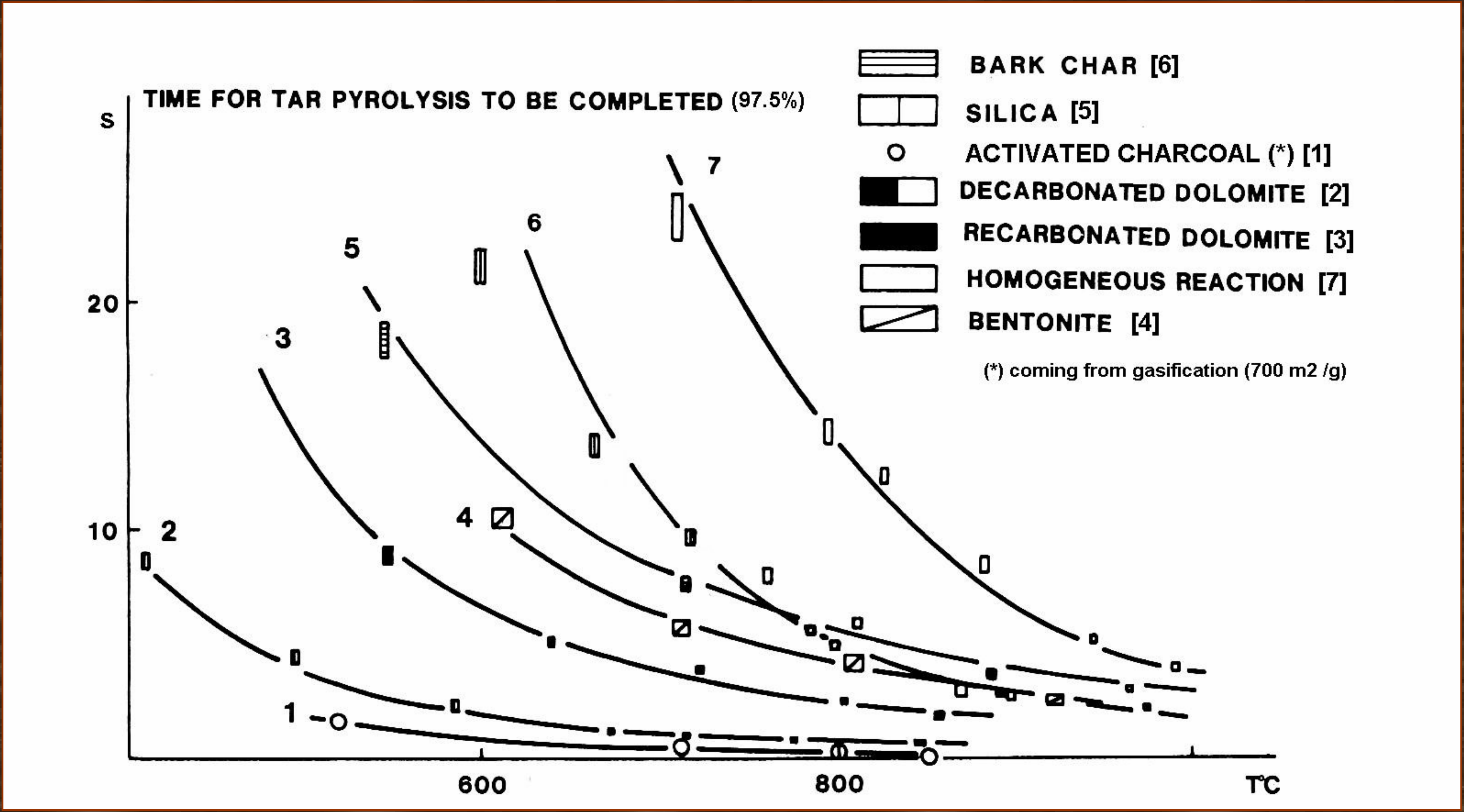
Medium BTU Gas (HHV around 16000 KJ/m^3)

But it was too early!





An important problem was the kinetics of Tar Cracking



LERMaB is coming back to fast pyrolysis to solve the problem of tar cracking, for the production of Syngas….with Gaz de France

Direct Hydrothermal Liquefaction

of wood, Hydrolysis Lignin elf, waste water treatment mud

Direct hydrothermal liquefaction involves converting Wood (sawdust, exploded chips) to an oily liquid (crude oil), in a pressurized reactor with CO.

✓ The reaction was:

$CO + \text{wood product} = CO_2 + \text{reduced wood}$

Wood react with CO, (in fact H_2 coming from a shift reaction, $CO+H_2O = CO_2+H_2$) in water at elevated temperatures (300-350°C) with sufficient pressure to maintain the water primarily in the liquid phase (12-20 MPa) for residence times up to 30 minutes.

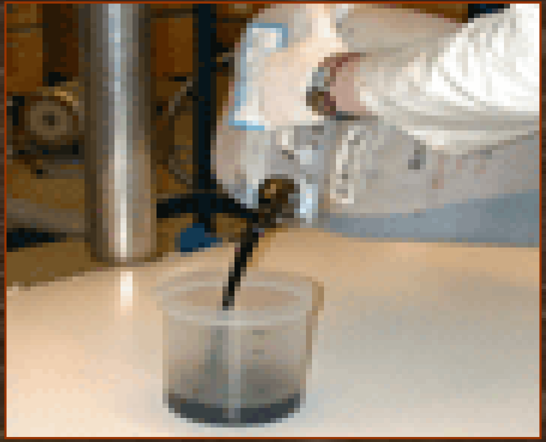
Direct Hydrothermal Liquefaction (continued)

The suggested mechanism was, with Na_2CO_3 as catalyst:

$$Na_2CO_3 + H_2 + 2CO \rightarrow 2HCOONa + CO_2$$
$$2C_6H_{10}O_5 + 2HCOONa \rightarrow 2C_2H_{10}O_4 + H_2O + CO_2 + Na_2CO_3$$

The overall approx. stoichiometry is: 100 Kg wood + 1 mol CO = 2.2 mol CO_2 + 1 mol H_2O + 55 Kg of non vapour product.

✓ oil yield was ~40% of dry wood feed with a rather high energy content, giving a high energy yield, ~ 65% of the HHV of wood.



Renewable Energy from Wood was not exactly Wood Science, but Chemical Engineering.

In the meantime, we have proceed to a survey of our expertise in Physical Chemistry with Walter Kauman to try to determine what was useful to develop a real research on Wood Material.

Being at the Board of Administrators of CTBA and with our expertise in kinetics, photochemistry, surface science,
we have chosen, topics of a real industrial interest:

- Wood adhesion and adhesives
- Wood photochemistry
- Wood durability and weathering,
- Wood finishing

Then a strong cooperation start with CTBA in Paris

Adhesion Adhesives

- This Topic has been developed with Daniel Masson

- Start with the application of theories of adhesion for the characterization of clean and aged (light, migration of extractives…) wood surface.

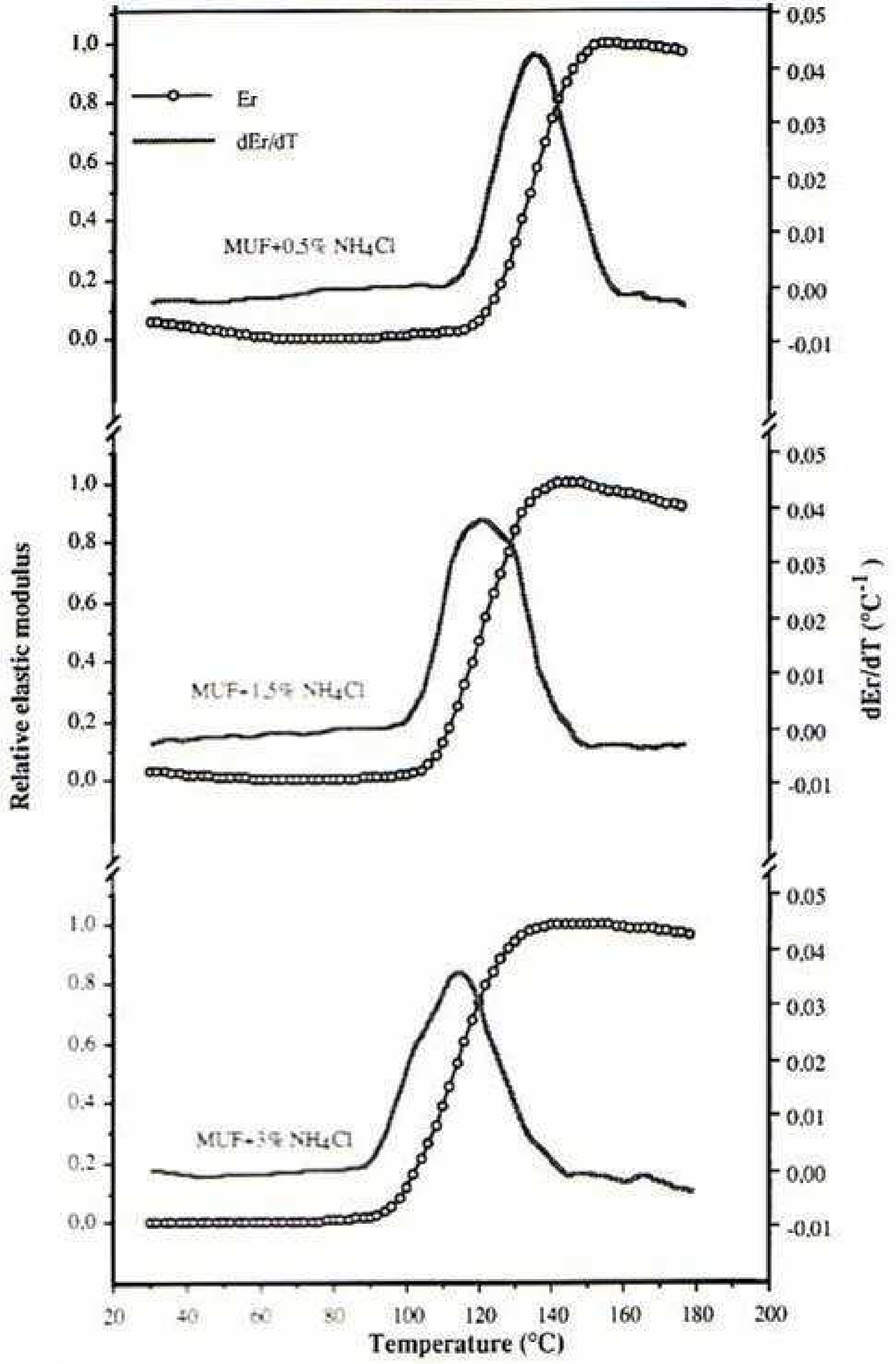
- Kinetics of Hydrolysis of UF resins by DSC (PhD Thesis of Dr. TSOU) for Orkem (formerly CDF-Chimie)

- Thermo chemical analysis of Wood/Amino/Plastic Adhesives joints cross-linking

DSC with kinetics analysis (Kissinger model) and TMA were applied to the characterization of amino plastic adhesives

Sample of TMA measurements

Evolution of the relative elastic modulus E_r and its first derivative dEr/dT of MUF/Wood joints as a function of temperature and hardener NH_4Cl

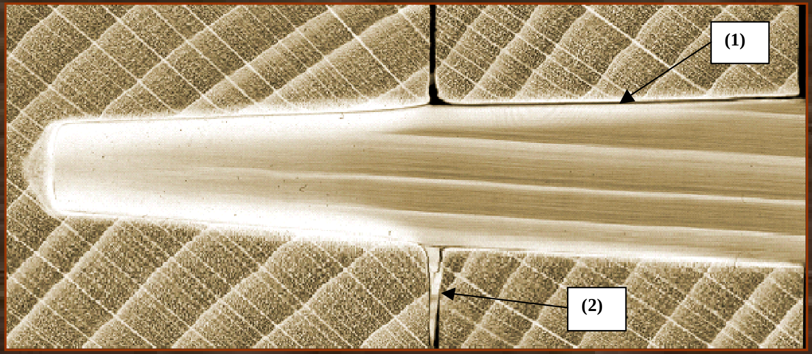


I met Tony Pizzi in 1985 in RSA and in 1992, in Taipei we discuss on a possible recruitment as Prof. in enstib

In 1994 Tony joined us.

And now it is another story!

He has transferred his strong expertise on adhesives in LERMaB and developed gluing without glue (Wood Welding)



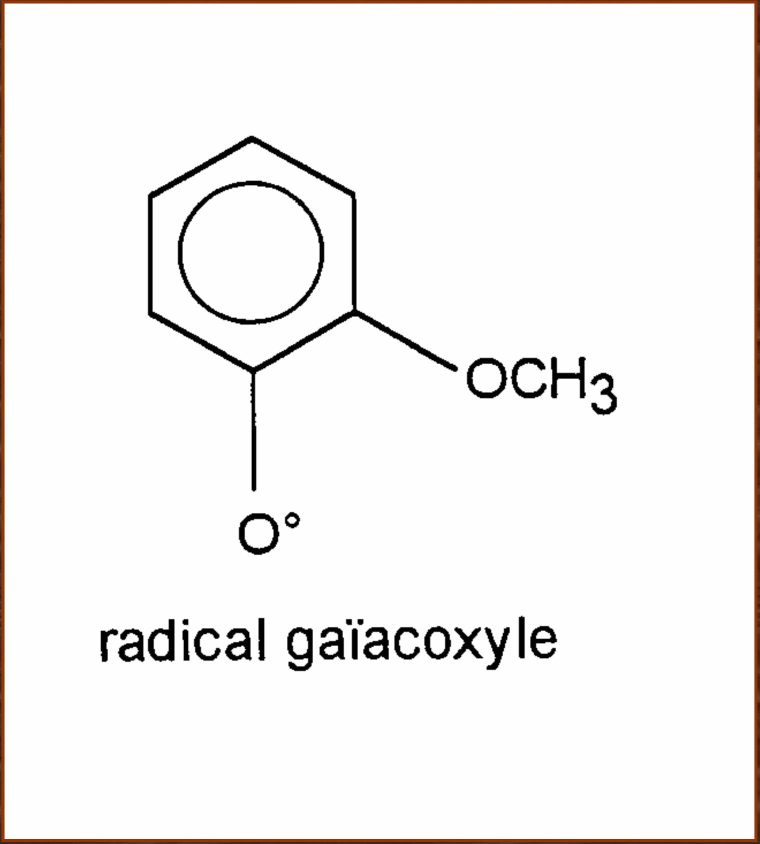
Wood "Photochemistry"

This domain is the heart of "our" Physical Chemistry
It is and has been strongly developed with
André MERLIN

Different topics have been studied:

- Mechanisms of Wood Photo-degradation
- Wood surface Color measurement
- Wood photo-stabilization with additives
  with pretreatment
- Wood finishes System Durability
- Influence of Tg
- Weathering (Natural and Accelerated)

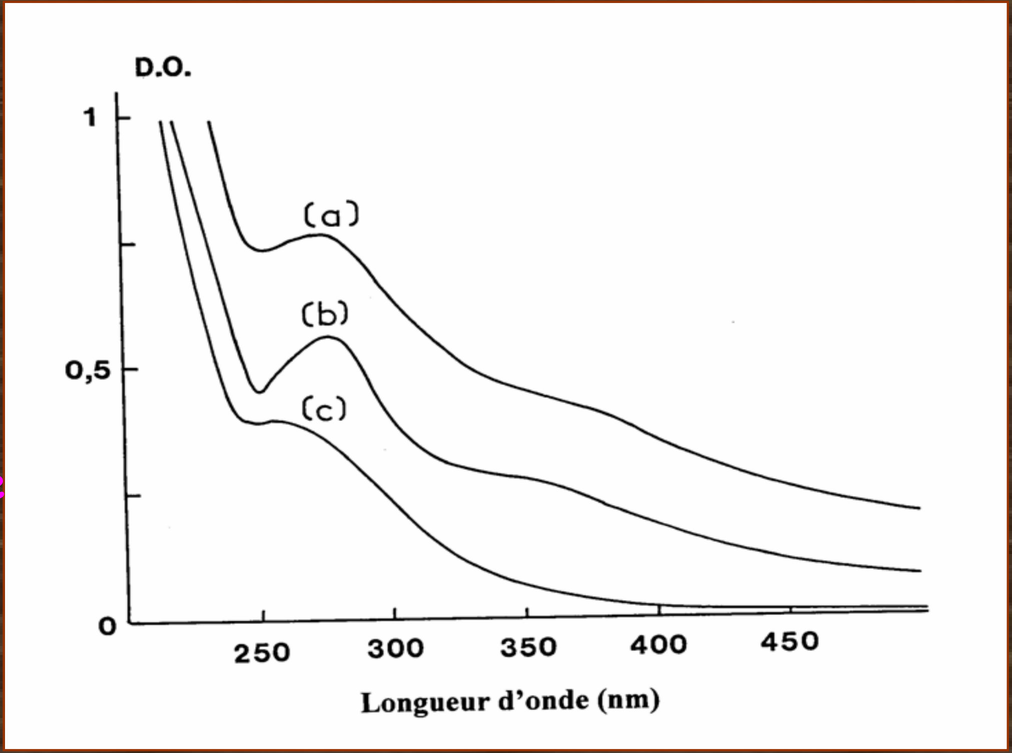
Molecular mechanism of the solar photodegradation of solid wood



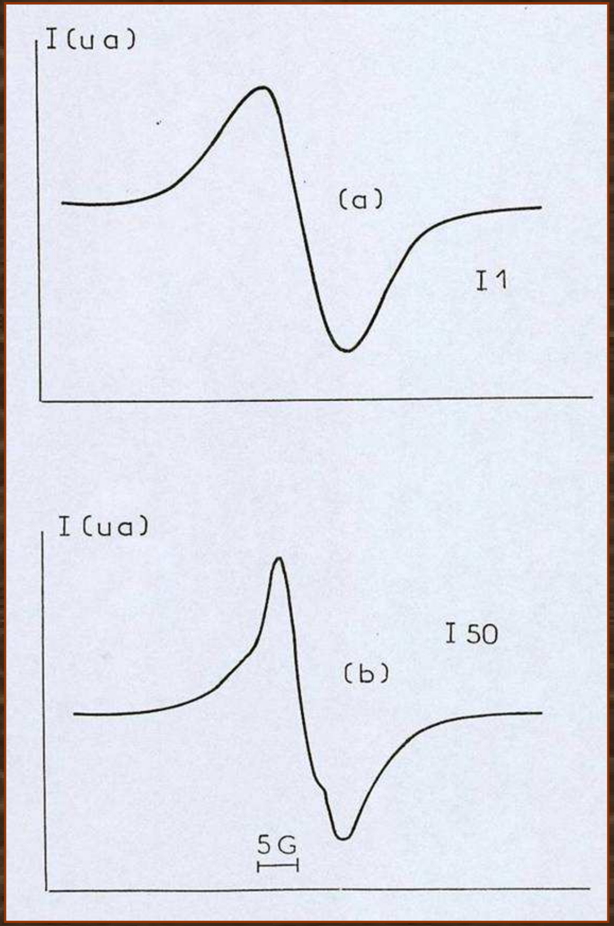
radical gaïacoxyle

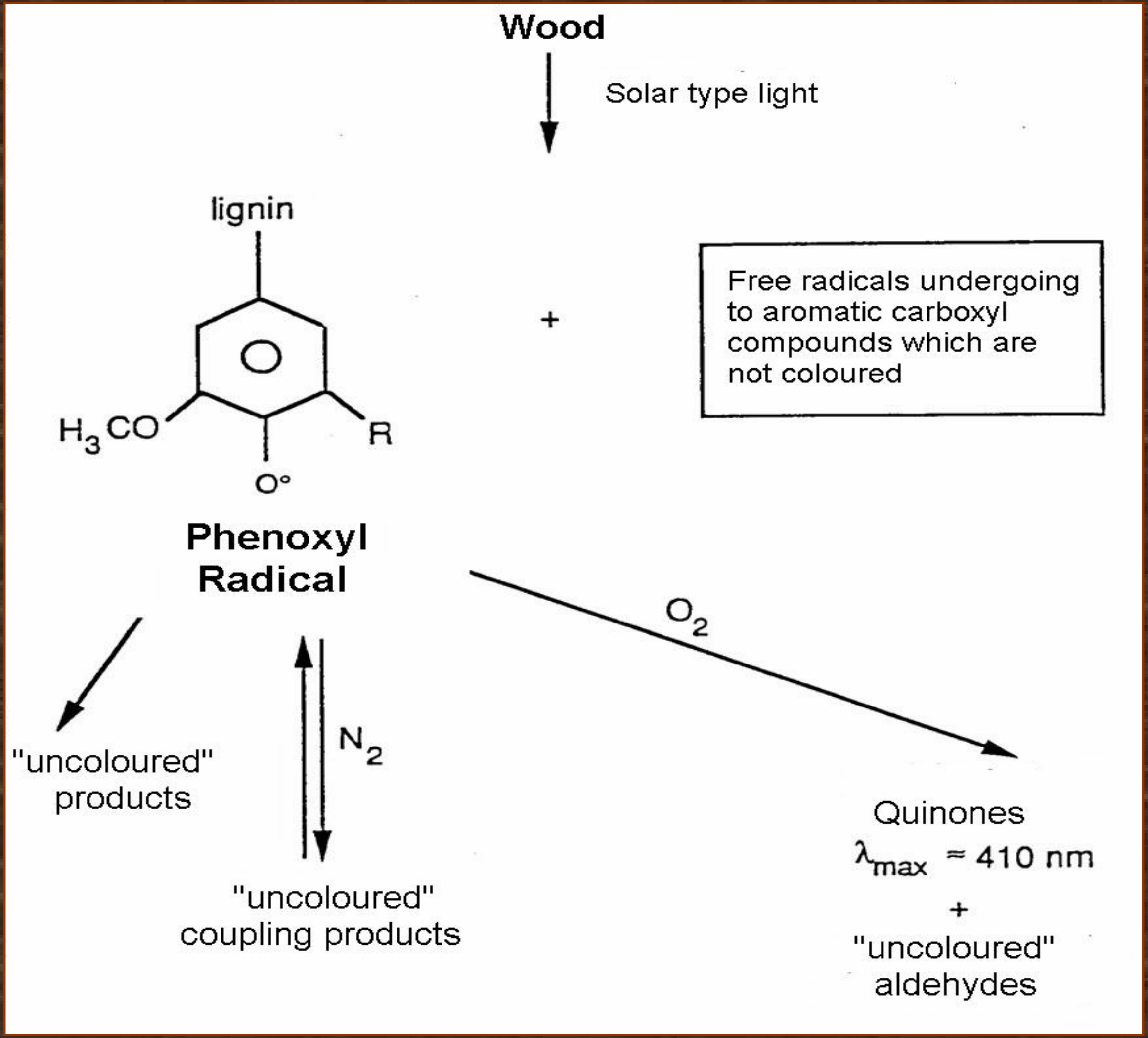
Photo discoloration (yellowing), first step of Wood photo degradation, exclusively due to this long lifetime phenoxy radical absorbing at 430nm

This radical is coming from lignin which absorbs UV and Vis light



Reflexion spectra :
(a) wood, (b) lignin's ,(c) cellulose





Wood

Solar type light

Phenoxyl Radical

Free radicals undergoing to aromatic carboxyl compounds which are not coloured

"uncoloured" products

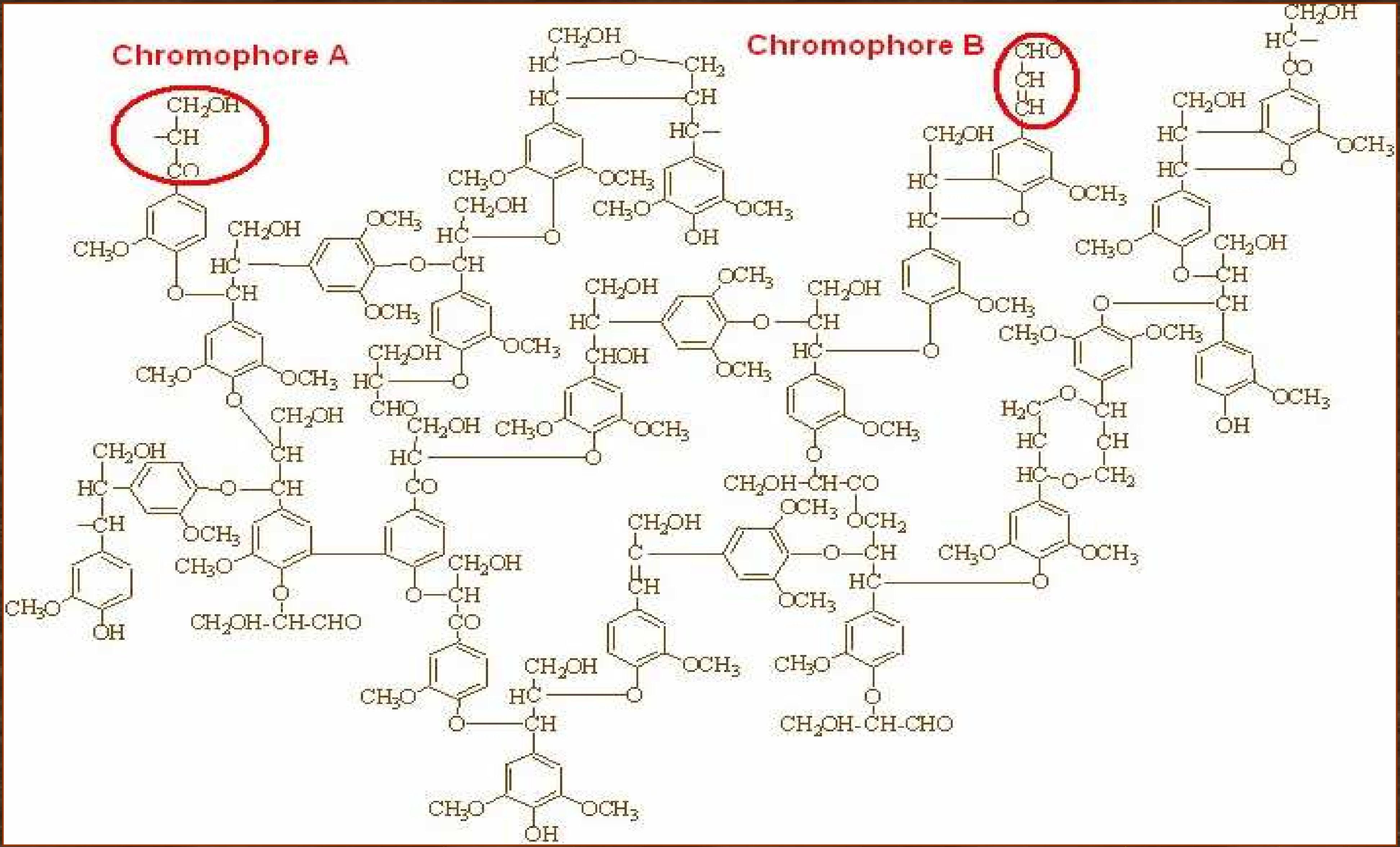
"uncoloured" coupling products

Quinones
$\lambda_{max} \approx 410$ nm
+
"uncoloured" aldehydes

ESR spectra of Fir (a) and Oak (b) after 90 minutes of irradiation:

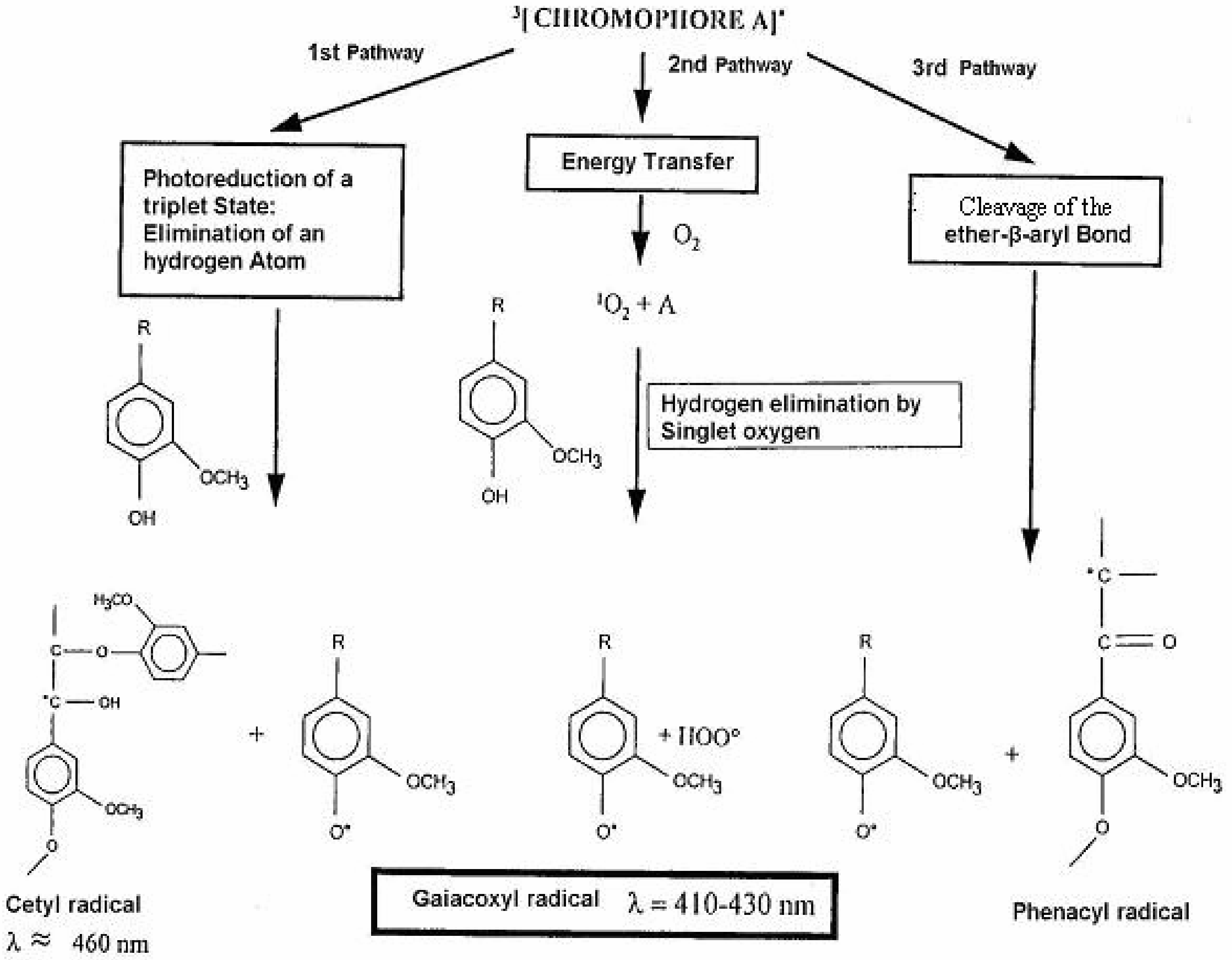
dissymetric signal combination of two singlets:

- phenoxy radical of lignins
- phenoxy radical of extractives



Partial structure of Softwood lignin

Chromophoric groups A and B are involved in the first step of the Photo-degradation of lignin and absorb UV (and Vis) Solar light.



$^3[\text{CHROMOPHORE A}]^*$

1st Pathway

2nd Pathway

3rd Pathway

Photoreduction of a triplet State: Elimination of an hydrogen Atom

Energy Transfer

O_2

$^1O_2 + A$

Hydrogen elimination by Singlet oxygen

Cleavage of the ether-β-aryl Bond

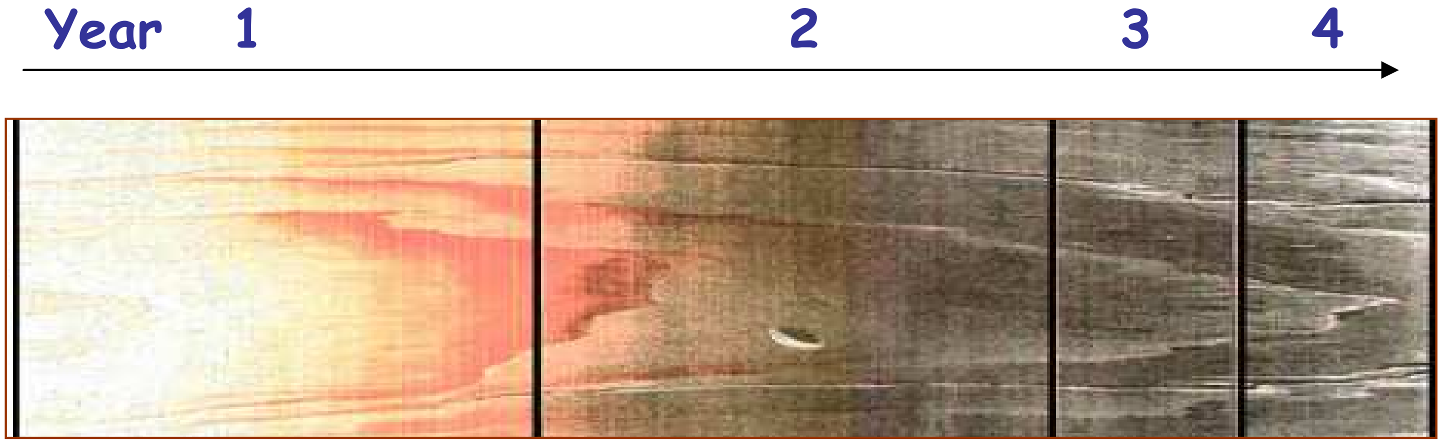
+ HOO°

Cetyl radical
λ ≈ 460 nm

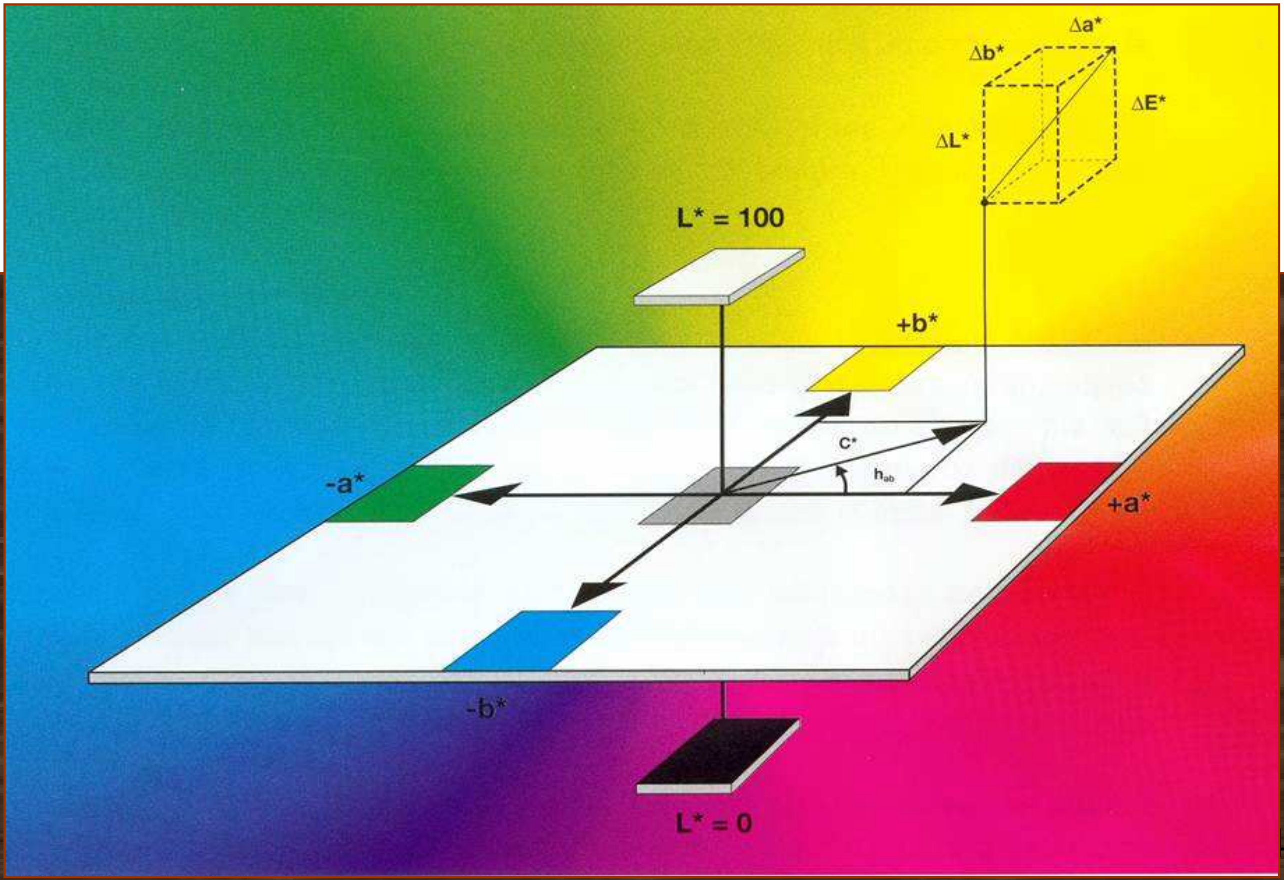
Gaiacoxyl radical λ = 410-430 nm

Phenacyl radical

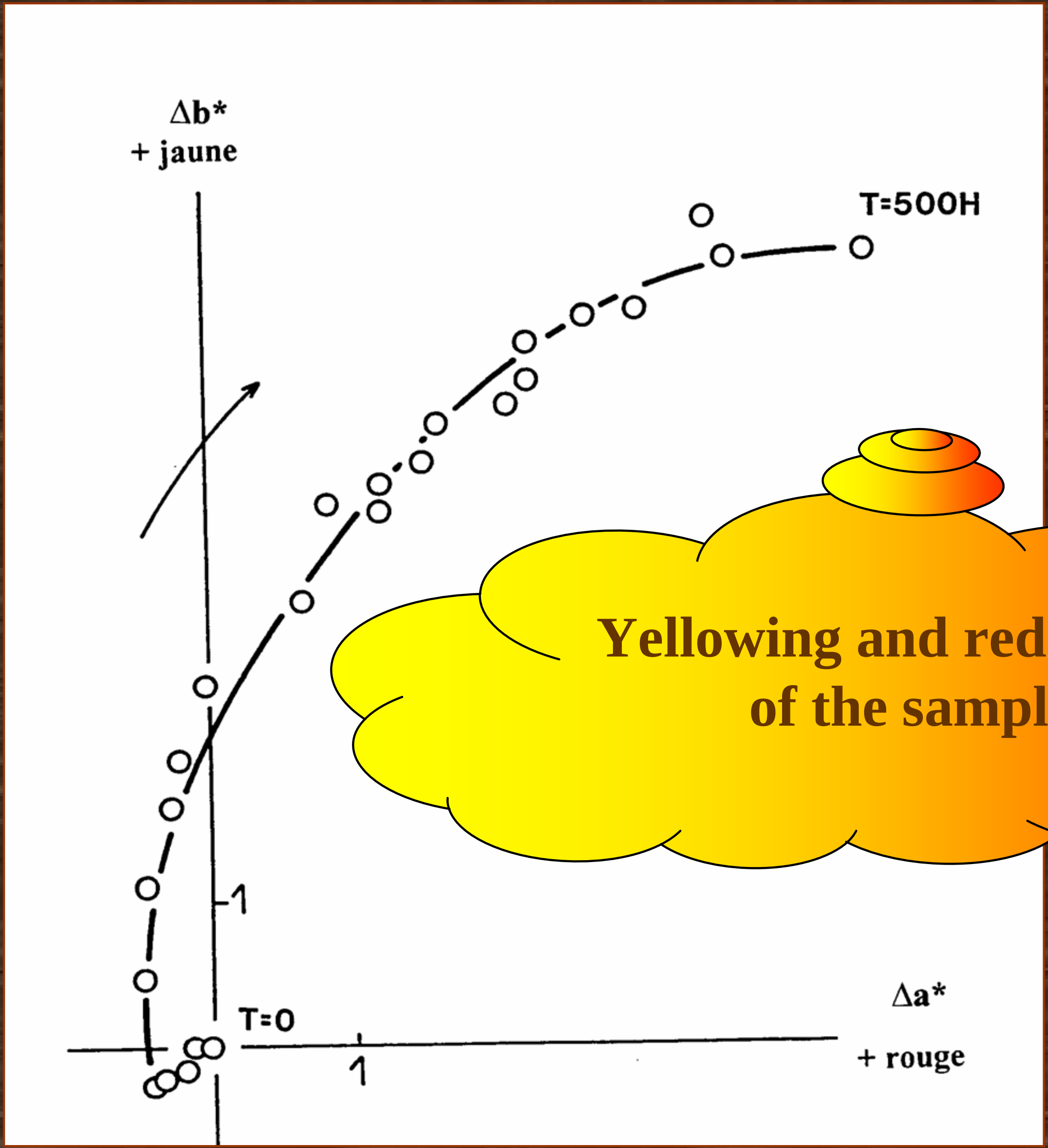
Natural color change for Softwood



Color measurement
With Cielab system

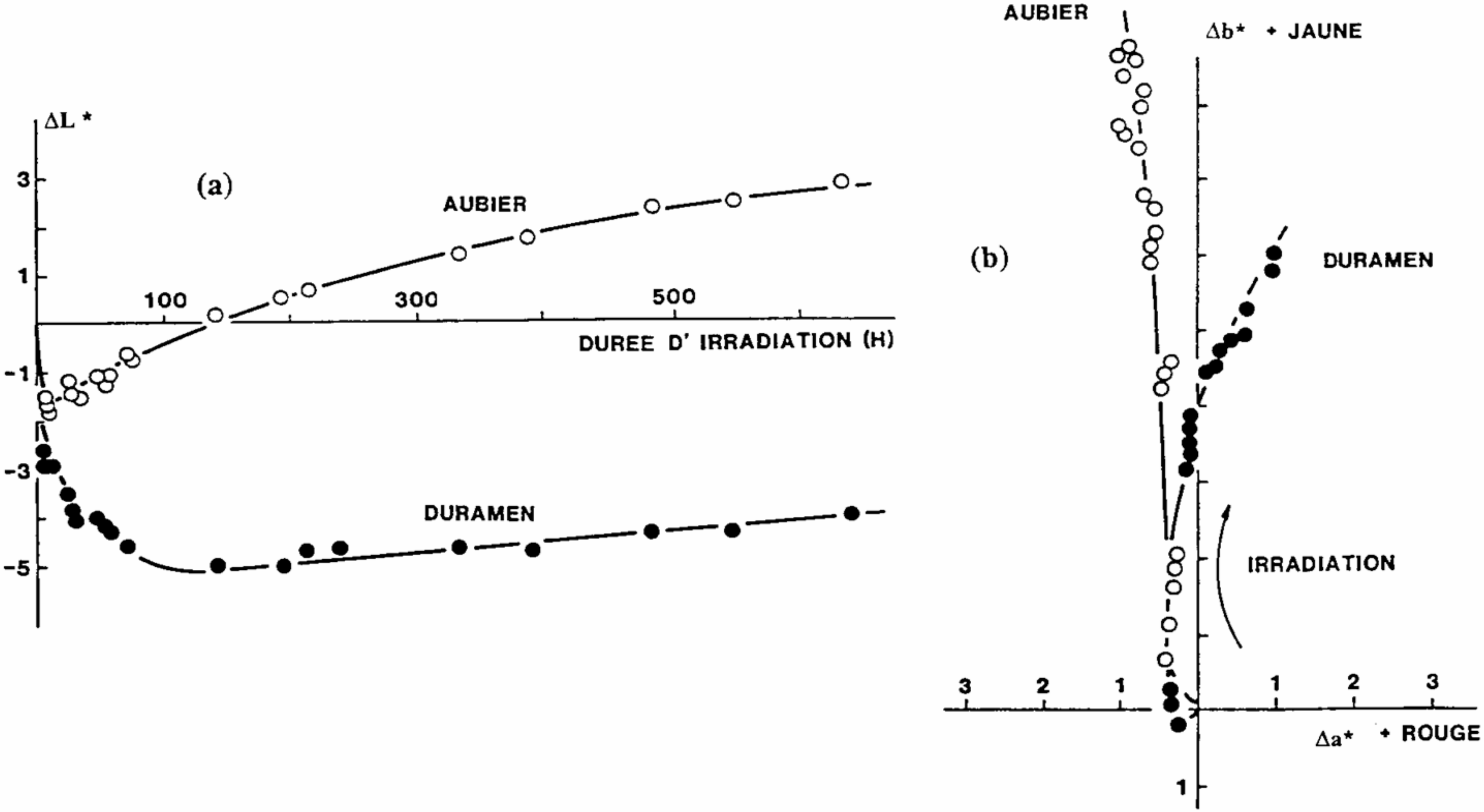


Color changes in the chromatic scale [a*,b*]



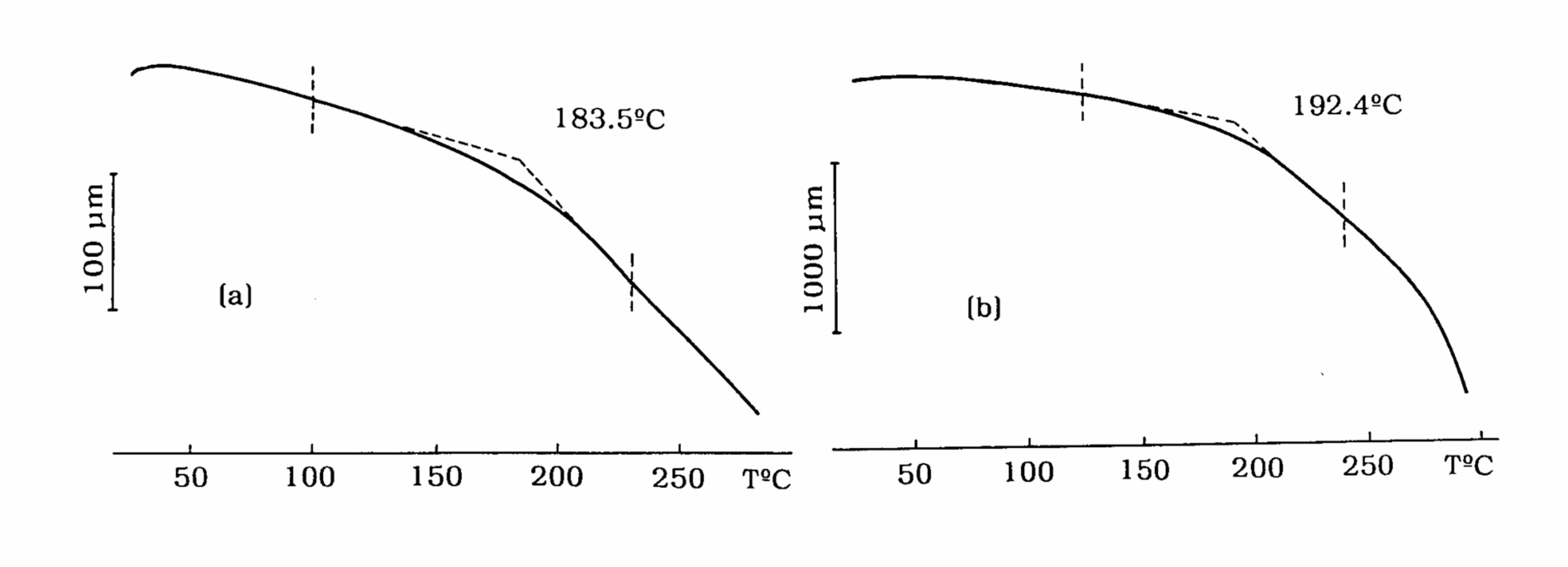
Yellowing and reddening of the sample

Oak photodiscoloration



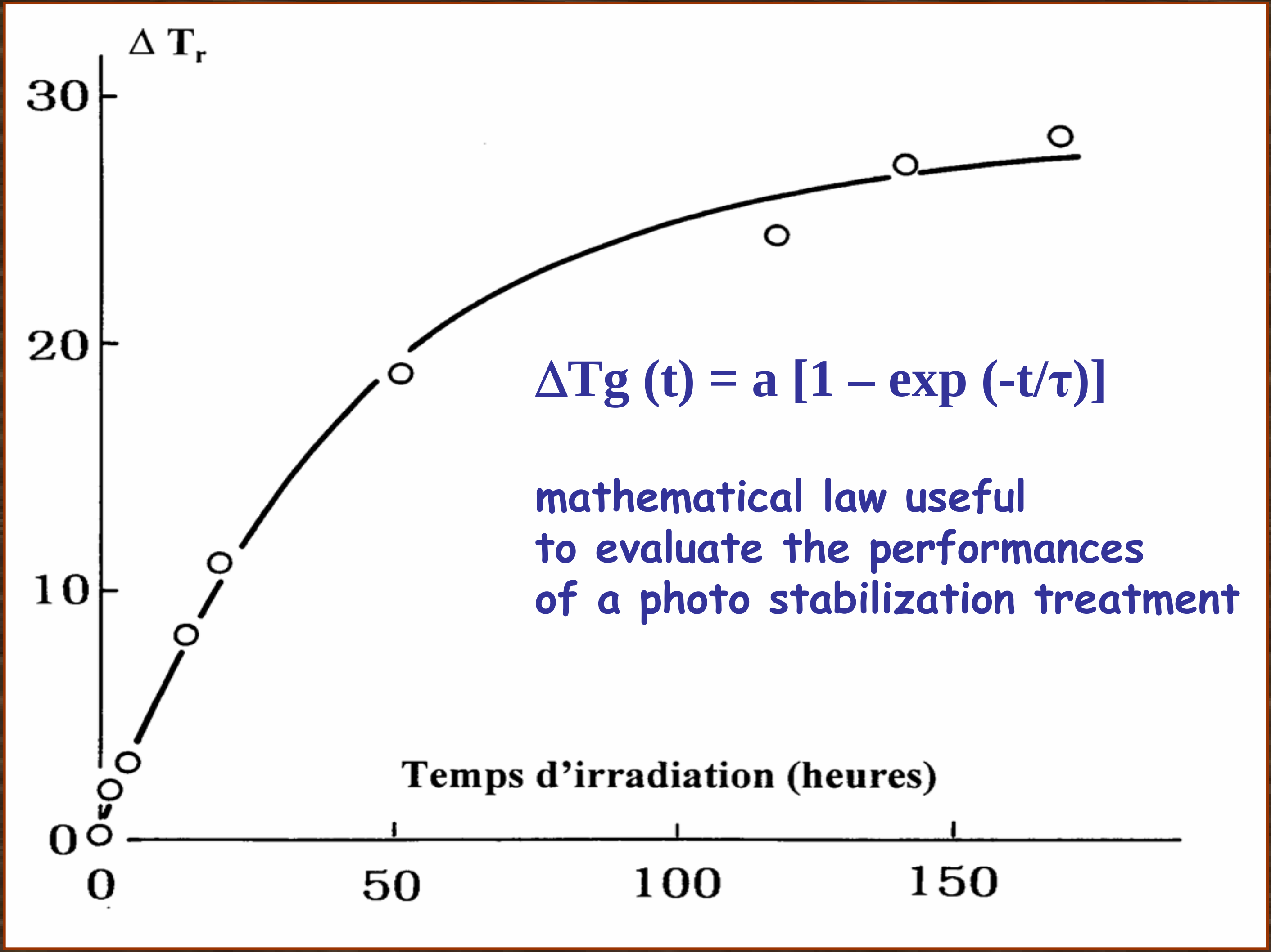
Different photochemical behavior of heartwood and sapwood

Viscoelastic properties of wood during weathering by thermomechanical analysis of a micro wood cut



(a) traction parallel to the fibers
(b) traction perpendicular to the fibers
Slope modification= Softening temperature of lignins

Softening temperature vs irradiation time



$$\Delta Tg\ (t) = a\ [1 - \exp\ (-t/\tau)]$$

mathematical law useful
to evaluate the performances
of a photo stabilization treatment

Remark: Tg is an excellent parameter to characterize the weathering of wood and Wood/finishes systems

Wood stabilization in outdoor conditions

Wood/finish systems are degraded during their outdoor exposure by UV, Heat, Oxygen and Wood dimensional variations due to water or humidity uptake.

In order to increase their durability different solutions have been proposed:

I. Apply a well formulated coating in clean conditions
II. Surface waterproofing
III. Photostabilization of Wood (Anti UV, UV Screeners, extractives from durable species)
IV. Wood thermal or Photochemical treatment
V. Permanent stabilization of wood by chemical modifications
VI. Photocuring wood surface composite

I-Apply a well formulated coating in clean conditions, on a stable wood where we have taken in account:

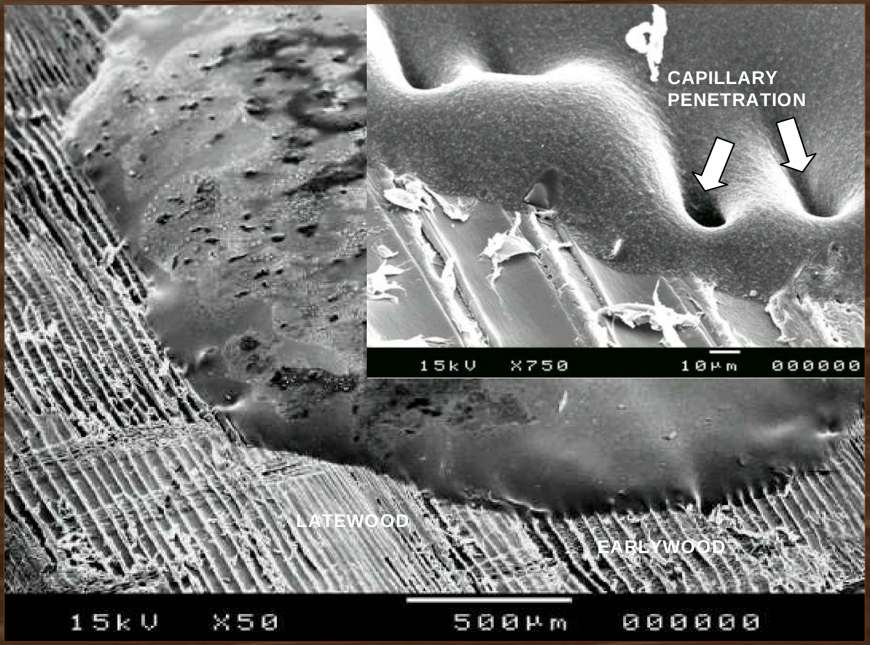
- Coating penetration into substrate
- Wood surface energy and wetting
- Adhesion
- Wood surface preparation
- Promoting adhesion (Corona)

Wetting, Wood surface energy and coating

- Viscosity can be limiting the wetting $\gamma_{coating} < \gamma_{wood}$
- Critical surface energy
- Polar and disperse components
- Van der Waals and (Lewis) acid-base components
- Young's equation:

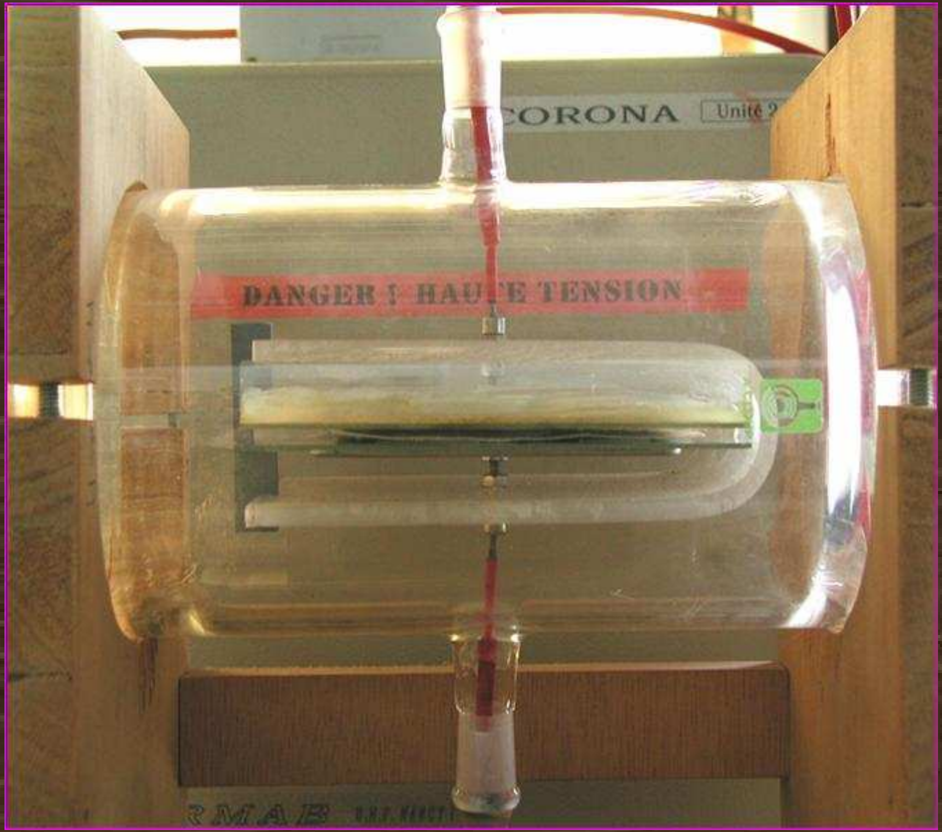
$$\gamma_s = \gamma_{sl} + \gamma_l \cos\theta$$

- Contact angle measurement with Drop or Wilhelmy plate with various liquids



II - Surface waterproofing by

- Plasma treatment with fluorinated or silicone compounds
- Corona treatment with ethylene giving a polyethylene film (Prof. UEHARA, Shimane Univ.)



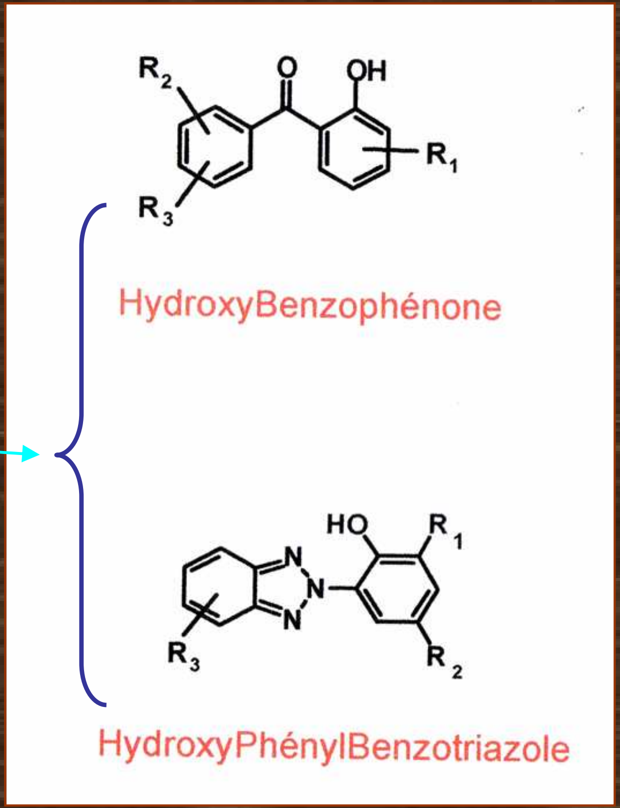
III – Photoprotection of Wood

To Prevent the wood surface from photodegradation and color changes by adding or grafting chemical products

UV Absorbers

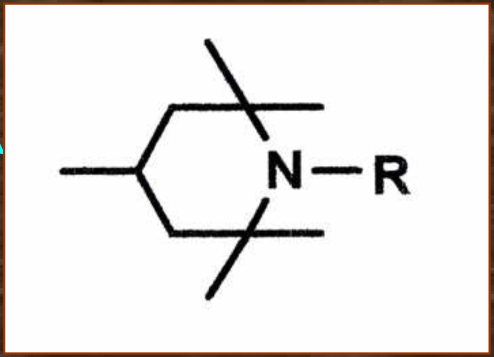
Hals (Hindred amines as light stabilizers

The antioxidants are not necessary,
as wood itself has antioxidant properties
with the polyphenolics extractives (tanins....)



HydroxyBenzophénone

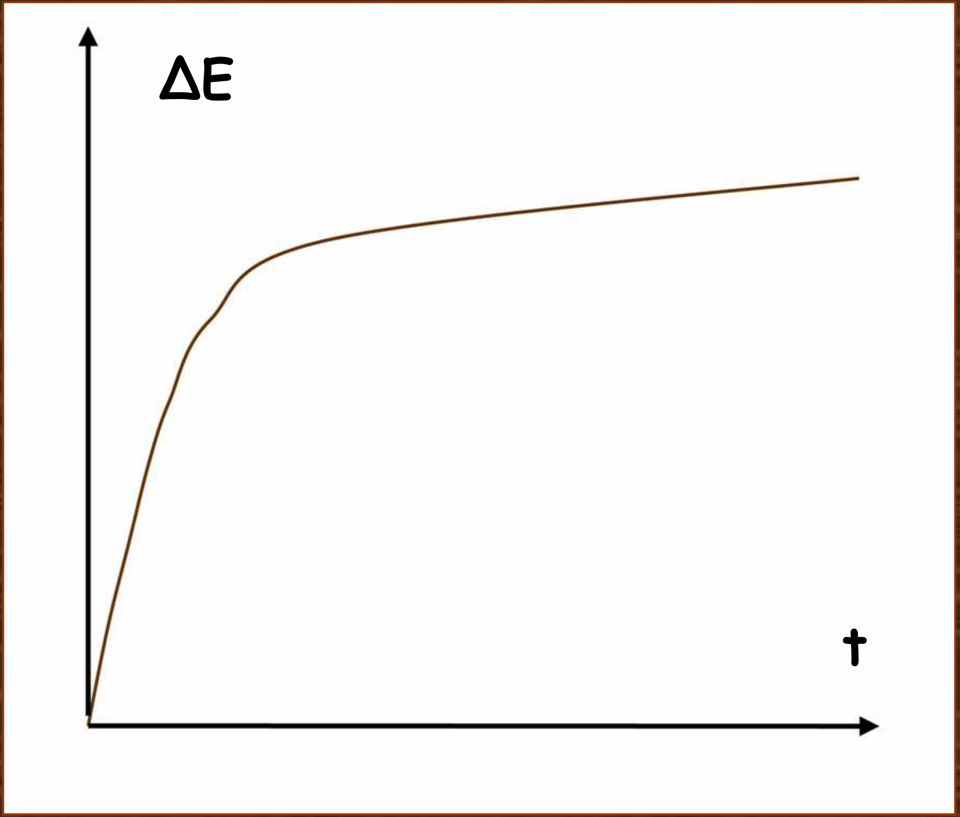
HydroxyPhénylBenzotriazole



IV - Wood thermal or Photochemical treatment

To obtain a stable aspect and colour, but darker.

Wood surface “stabilization” by pre-weathering

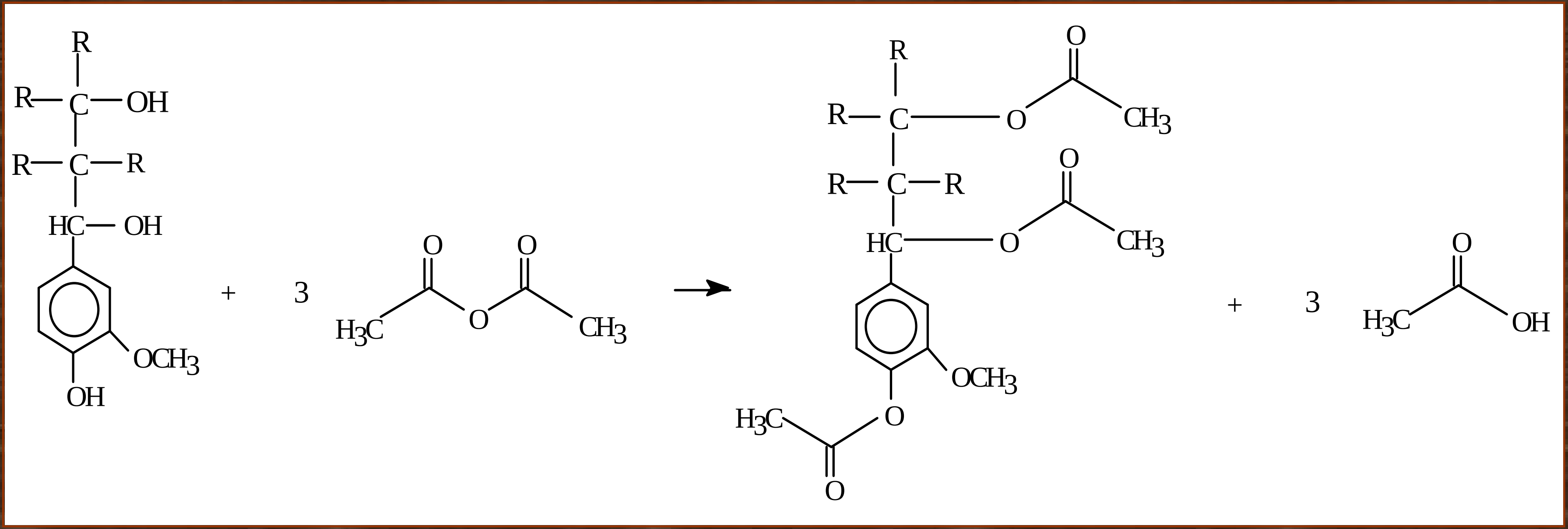


- Surface impregnation with an equimolar mixture of MDEA (Benzophenone/Amine)
- Irradiation 1 hour (15 mW/cm^2 at 360 nm) equivalent to a 500hours of photoirradiation (5mW/cm2 at 360nm)

The result is a stabilization of the wood color

V - Permanent stabilization of wood by chemical modifications

to prevent it from dimensional variations and surface photodegradation of lignin by, for example, acetylating of hydroxyl groups in the aliphatic and the aromatic part of the lignin and hydroxyl groups of cellulose

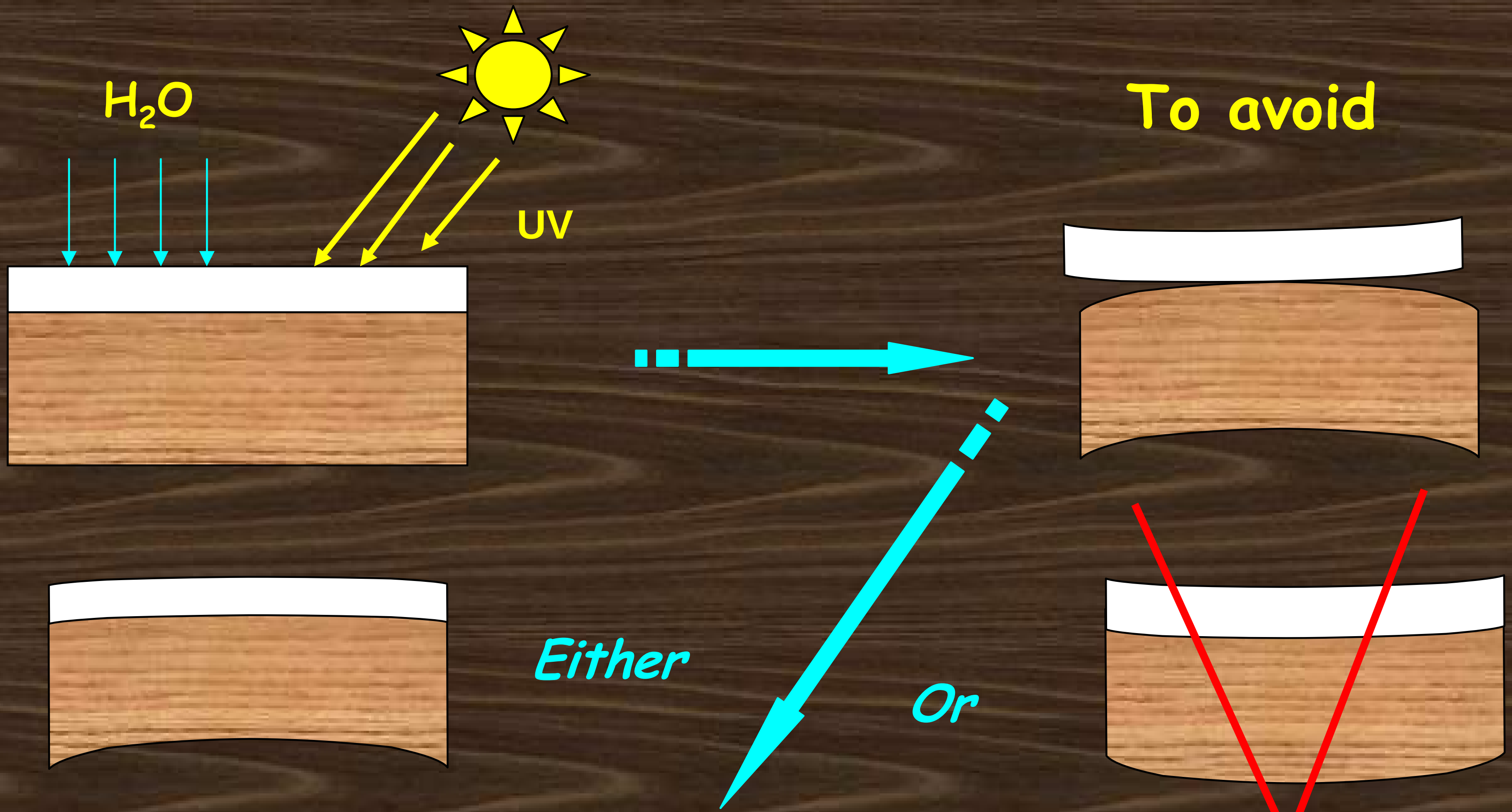


Most of our proposals have been applied by Ciba

Main problem is the price, for a 10 years Warranty!

VI – “Photocuring wood surface composite”

In order to increase the durability of the wood/finish system, we have proposed a new way of stabilization by considering the Tg of the two parts of the system: wood substrate and finish.



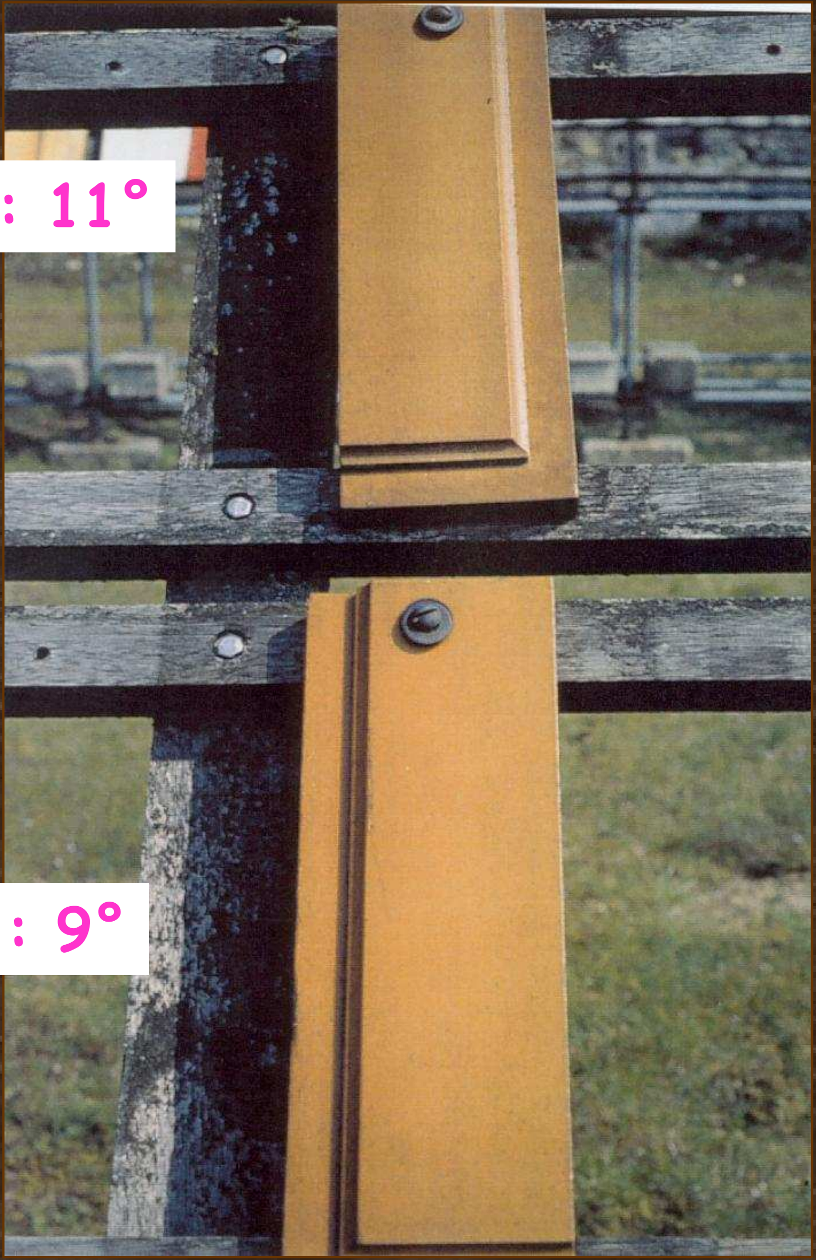
low Tg of the finish < T°$_{use}$

~~Tg of the substrate low~~

Formulation of a soft finishing

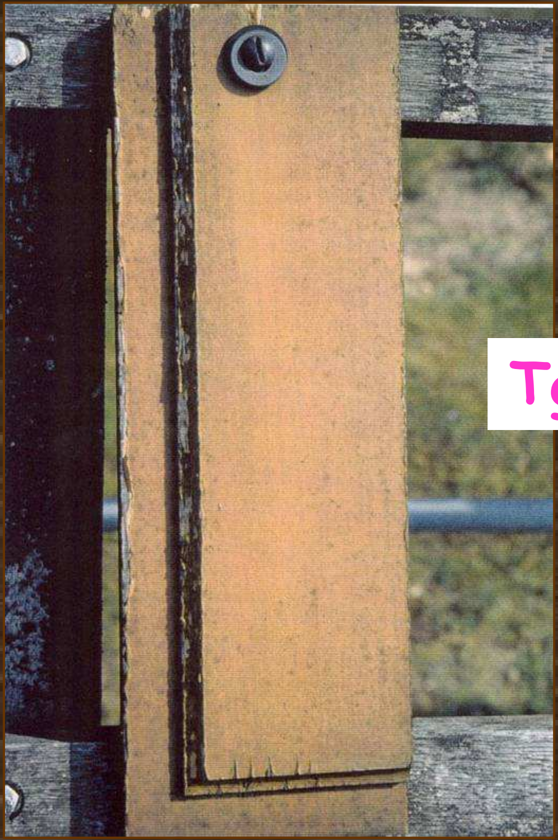
~~Softness of the substrate!~~

Relationship Tg vs durability: 24 months natural weathering, CTBA tests



Tg : 11°

Tg : 9°

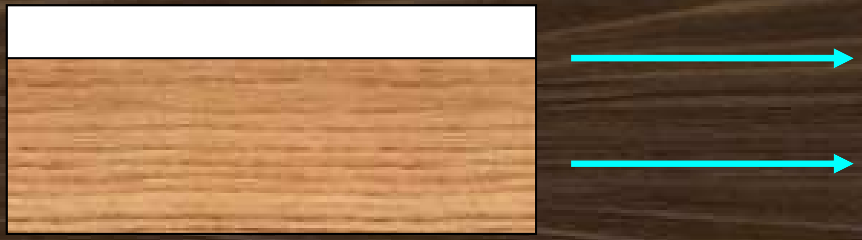


Tg : 36°

T_{ext} > Tg to keep the flexibility of the coat

T_{ext} > Tg Tacking effect

THE BEST SOLUTION



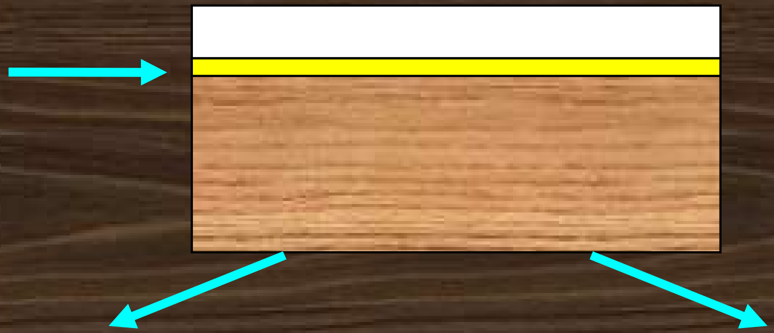
Finish : durability / softness

Dimensional stabilization of wood

NOT EASILY OBTAINED WITH A SUBSTRATE LIKE WOOD

OUR PROPOSAL :

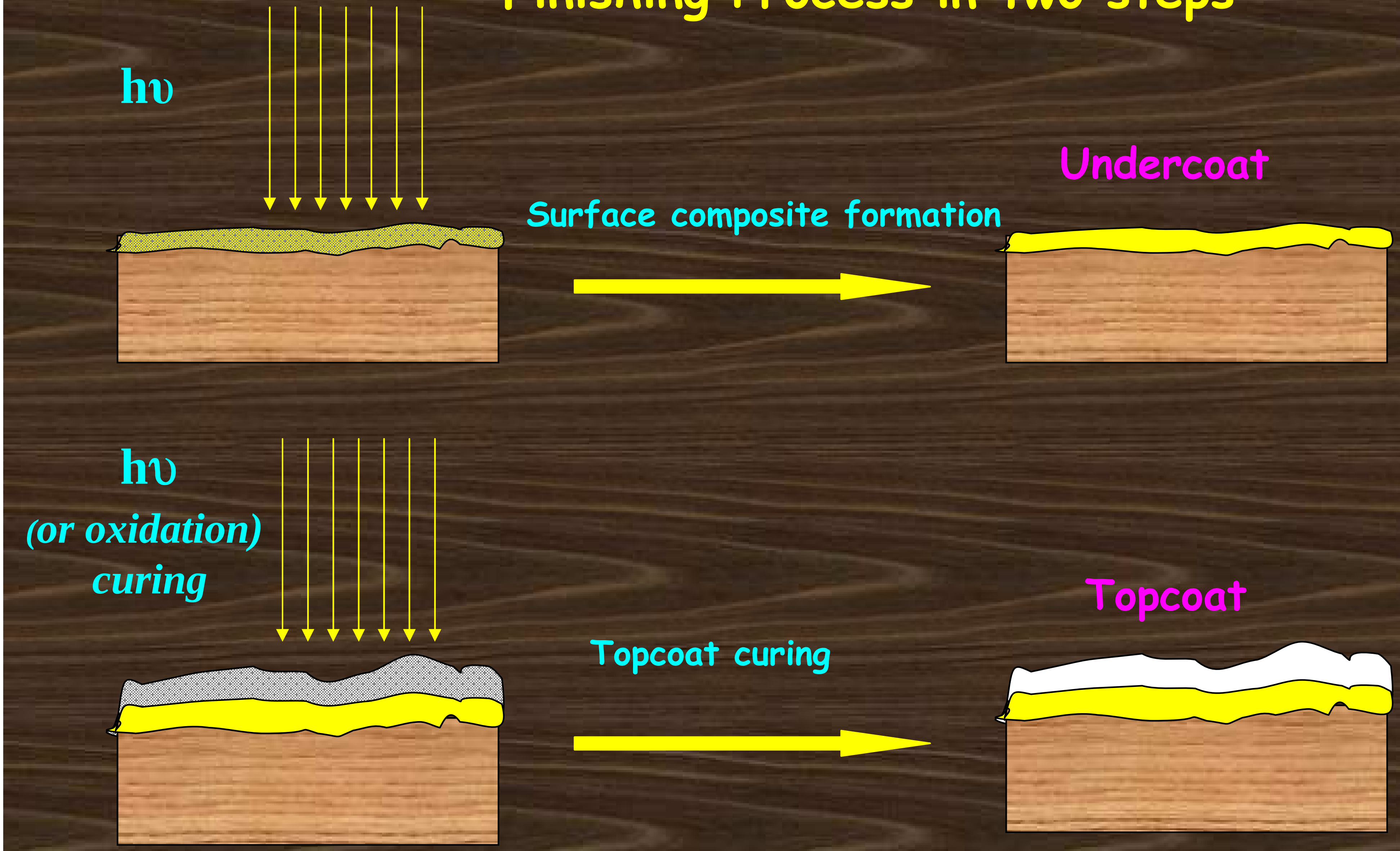
Flexible undercoat



Lowering of wood dimensional variations and absorb the solicitations on the topcoat

Improvement of the anchorage of the topcoat by an enhancement of the chemical compatibility between undercoat and topcoat

Finishing Process in two steps



hυ

Surface composite formation

Undercoat

hυ

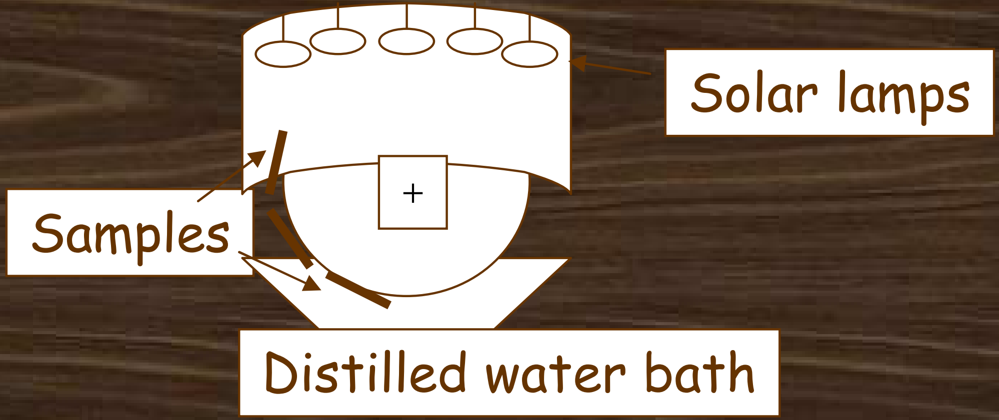
(or oxidation)

curing

Topcoat curing

Topcoat

Weathering : Gardner type degradation wheel and QUV



- Adhesion : X cut of cross-hedge test *(NFT 30-038)*
- Measurement of the peeling force of an adhesive tape, TMA

SELECTED SYSTEM

Topcoat

Alkyd or acrylic

Acrylate undercoat :

TMPTA

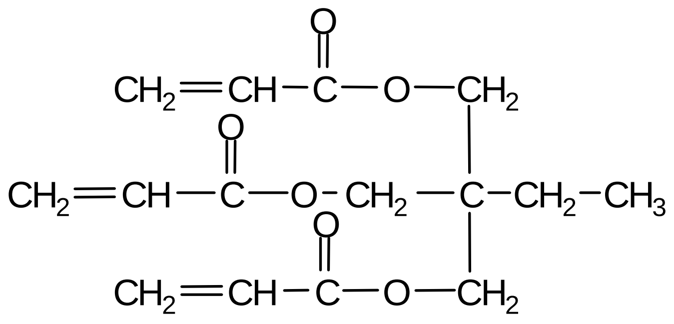
(trimethylolpropanetriacrylate)

or

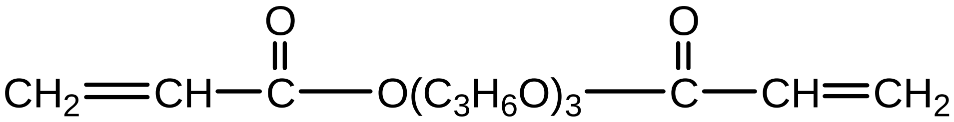
TPGDA (tripropaneglycoldiacrylate)

Substrate :

spruce, oak or beech



TMPTA



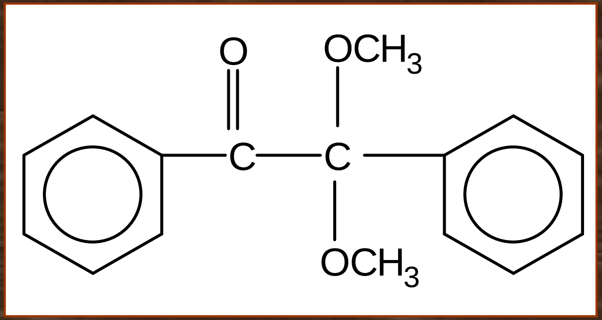
$$CH_2{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O(C_3H_6O)_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH{=}CH_2$$

TPGDA

Reference *: wood substrate + 2 alkyd coats*

Polymerization process for the undercoat :
PHOTOCHEMICAL INITIATION
with DMPA *(dimethoxyphenylacetophenone)*

is it a chemical modification
or a physicochemical modification ?



Formation of a wood/polymer composite
limited to the sample surface
High curing rates
Rather low temperature curing
Easy control of cross linking ratio

X cut of cross-hedge test Results

Undercoat	TMPTA	TPGDA	Alkyd
Topcoat	Alkyd	Alkyd	Alkyd
Before ageing	XXX	XXX	XXXX
After ageing	XX	X	Lixiviation

% of squares released after weathering (Gardner wheel)
x : bad, XX : poor, XXX : good, XXXX : excellent

Limiting factor: interface between undercoat / topcoat
No flakes observed but layers set apart

FLEXURE RESISTANCE MEASURED BY THERMOMECHANICAL ANALYSIS

	Deflexion (μm)	Flexure resistance kN/μm	Relative flexibility *
Wood without treatment	114	$3,5.10^{-3}$	2,32
Wood treated with TMPTA	63	$6,3.10^{-3}$	1,28
Wood treated with TPGDA	49	$8,2.10^{-3}$	1

* Calculated with TPGDA system as a reference

TMPTA > TPGDA

Last topics under development are:

1. Vis Photochemical curing of varnishes and paints
2. Role of phenolic moieties on cross-linking of varnishes: Inhibition by phenol extractives
3. Understand why some species are durable

Dominique Perrin who joined LERMaB in 2000, compares the antioxidant capacities of extractives coming from durable species, by using the oxidation of an unsaturated oil with model antioxidant (α-tocopherol).

Some of these extractives (Yellow Birch) have interesting nutracetic properties, cooperation with Prof. Tatiana Stevanovic (Laval University)

Remark: There is a long-lasting with Laval and now with its CRB (Wood research Center) LERMaB and CRB are working quite on the same topics!

Conclusion

- You have had a short overview of 25 years of research for Wood.

- In our country Research is always a “team work”. I am not sure that it is the best way to progress. But we need individualities to develop new and crazy concepts!

- “Physical Chemistry” is really the basis of understanding wood properties, processes (adhesion, protection, durability, artificial weathering…).

- With Genetics and Silviculture, “Physical Chemistry” is the best way to: upgrade the properties and qualities of Wood and inventing new materials …with Wood which will be very expensive in the future!

- “Physical Chemistry” allows the transformation of wood wastes into valuable feedstock…for Energy!

Conclusion (cont'd)

Never forget these two rules

Food > Feed > Fuel

3F Rule for Bioenergy!

Food > Fine chemicals > Feed > Fibers > Frame > Fuel

6F Rule for Wood!

And think to recovered Wood

Further information about Cost Action E31 see

http://www.ctib-tchn.be/coste31/frames/F_e31.htm

Hopefully it was not too boring!

Thanks for your attention
Questions ?

谢谢您听
问题 ？
再见