

Wood preservation by a mixed anhydride treatment

Using simple models of polymeric wood components for an ^{13}C NMR investigation

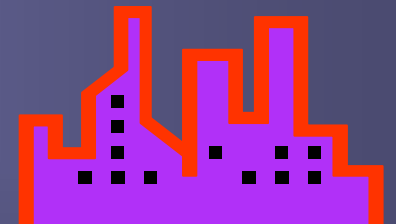
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Wood modification

- ★ Wood treatment with acetic anhydride or another anhydride
→ Not new
- ★ Improvement of wood dimensional stability and resistance to decay
- ★ Production & Commercialisation of such modified wood





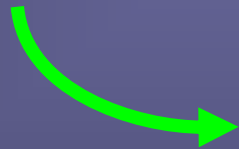
Wood modification

- ★ Recently, a novel approach was reported

Magne et al (2006)

European patent application EP 1 657 231 A1

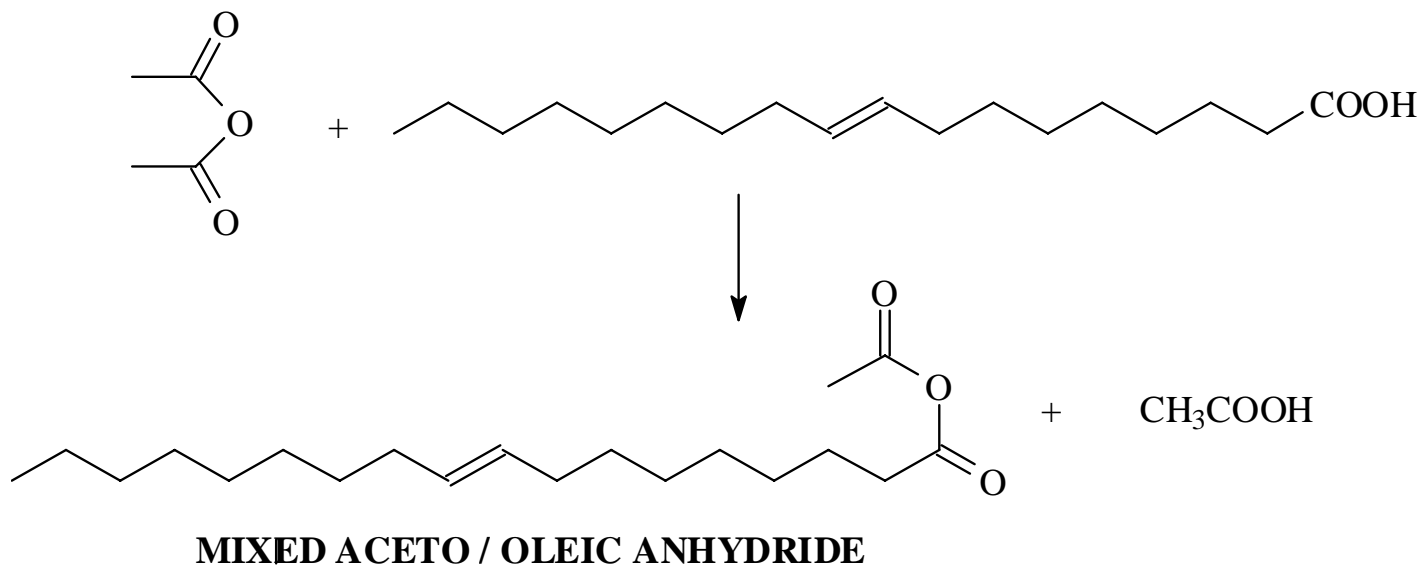
- ★ Reaction between an acetic anhydride and a fatty acid up to C24-length chain



Such as oleic acid C20



Reaction



Obtention of a mixed aceto-oleic anhydride

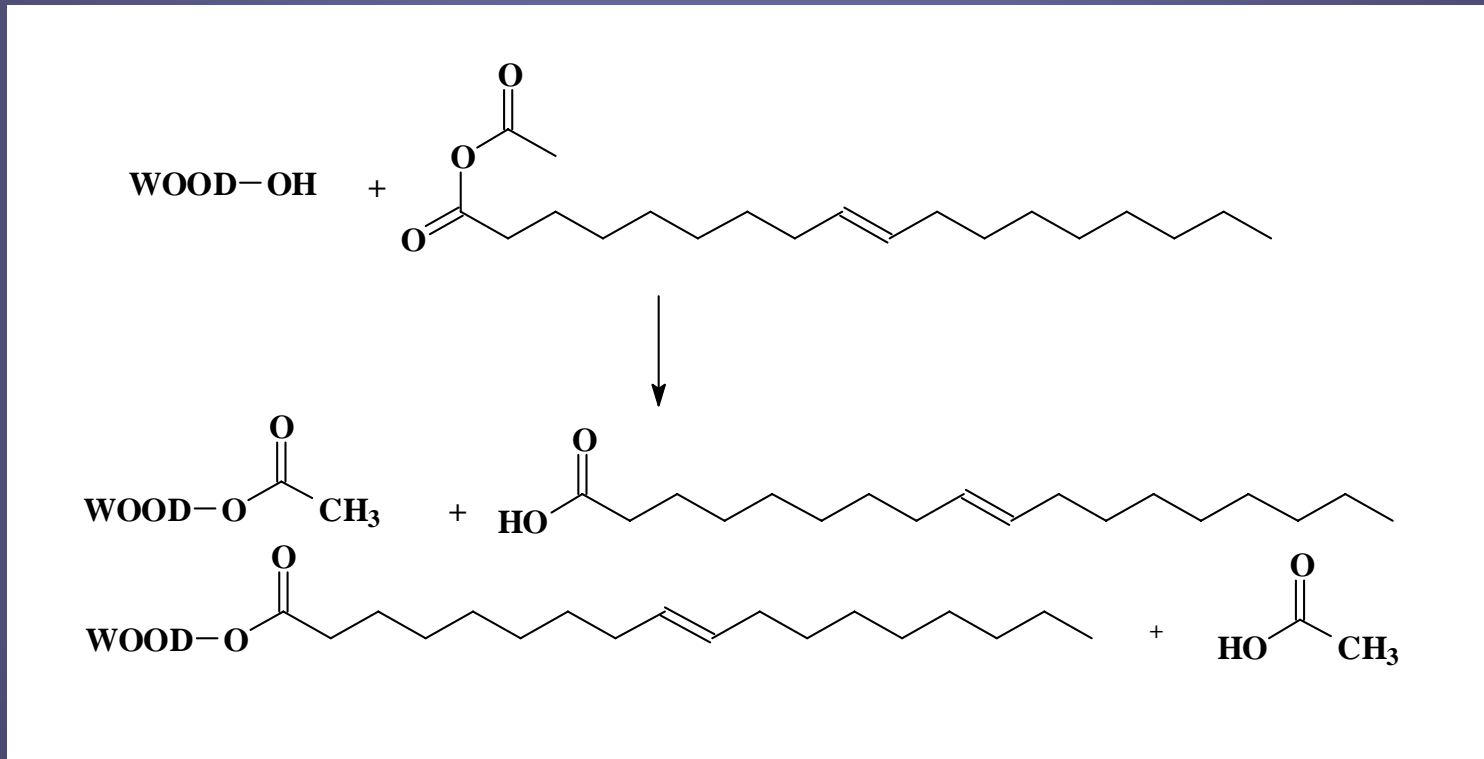


Reactions with wood

Reactions of the mixed aceto-oleic anhydride with wood

★ Acetylation

★ « Oleification »





Reactions with wood

★ Acetylation



Dimensional stability
+
Protection against decay

★ « Oleification »



Fixation by
esterification
would improve
water repellence



★ Patent - Magne et al, 2006

Esterification by the oleic acid residue was not checked in situ but by indirect methods

★ Florent Lyon, Ph. D work

(Boric acid + oil) wood treatment

Synthesis

Boric acid (+ ammonia) + oleic acid

= Ammonium borate oleate

to treat the wood



- ✦ Considering this new approach
- ✦ Does aceto/oleic anhydride form ?
- ✦ If yes :
Yield ?
Fixation onto the wood ?
- ✦ Can another type of anhydride be used to prepare a mixed anhydride of similar type ?



Experimentals

- ★ Mixed aceto-oleic anhydride
1 mol. Acetic anhydride + 1 mol. Oleic acid
 $T^{\circ} = 20^{\circ}\text{C}$ to 140°C
Time = 20 min to 30 min
+/- Addition = H_2SO_4 , pyridine traces
- ★ Simple models used for the wood
Glucose \longrightarrow Cellulose
Guaiacol \longrightarrow Lignin



Experimentals

- ★ 7 Reactions of raw mixed anhydride on glucose or guaiacol

temperature, time, +/- pyridine
water solutions or solid state

- ★ 2 Transesterification reactions
(Mixed anhydride + model) + ethyl oleate

- ★ 8 Other reactions
Glucose + oleic acid/ethyl oleate

temperature, time
water solutions or solid state



Experimentals

- ★ Analysis of the obtained products
- ★ Liquid phase ^{13}C NMR
- ★ Solid state MAS-DES(proton decoupling)
 ^{13}C NMR



Results

- ★ Mixed anhydride does indeed form
- ★ Considerable amount of oleic acid is not converted into anhydride and is left unreacted
- ★ NMR also quantitative
Comparison of integrated areas



Results

140°C
H₂SO₄
30 min

140°C
Pyridine
30 min

140°C
-
30 min

20°C
-
1 hr

Oleic acid 13%

13%

11%

14%

Acetic acid 30%

30%

28%

33%

Acetic anh. 22%

22%

21%

21%

Mixed anh. 35%

35%

39%

32%





Results

- ★ Guaiacol
Guaiacyl nuclei of lignin gets esterified
But forms exclusively the acetate ester
- ★ Presence of only one ester
= all mixed anhydride reacts
= but is rather unstable and undergoes
the reaction
- ★ Oleic acid → Mixed anhydride (yield)
This mix reacts with a simple lignin model
+ at the end reverts fixation
Remain as free oleic acid



Results



Glucose

Little esterification was shown



Conclusion

- ★ Aceto-oleic anhydride can be formed
- ★ When used to treat wood
= is rather labile and unstable
- ★ Leaves large amounts of free oleic acid
Into the treated wood
 - Leak out of the wood
 - Compatibility with coatings