AGROTECHNOLOGY & FOOD INNOVATIONS
WAGENINGEN UR

New non-food technologies using (un)saturated and hydroxy functionalised fatty acids

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Introduction

Common oils and oil yields

Oil Source	Oil yield (%)
Cotton seed	18
Corn	45
Peanut	35
Soy bean	18
Safflower	28
Sunflower	25
Coconut	63
Palm Kernel	45
Castor	20
Linseed	45
Tung	34
Inedible tallow	60-90

Ref: Oleochemicals as feedstock for the Biorefinery, Joe Bozell, NREL, August 2004

Introduction

US 2000 consumption of fatty acid (derivatives)

Consumption of fatty acid (derivatives)	Consumption (10^6 lb) 2000
Personal Care products	631
Industrial lubricants, corrosion,oilfield	292
Plastics	266
Cleaners	251
Coatings and Adhesives	184
Fabric softeners	184
Emulsion polymers	102
Foods	92
Rubber	86
Paper	81
Candles, waxes	59
Mining	40
Textiles	34
Asphalt	34
Buffing compounds	25
Agricultural	22
Exports	92
Other	84
Total	2615

Ref: Oleochemicals as feedstock for the Biorefinery, Joe Bozell, NREL, August 2004

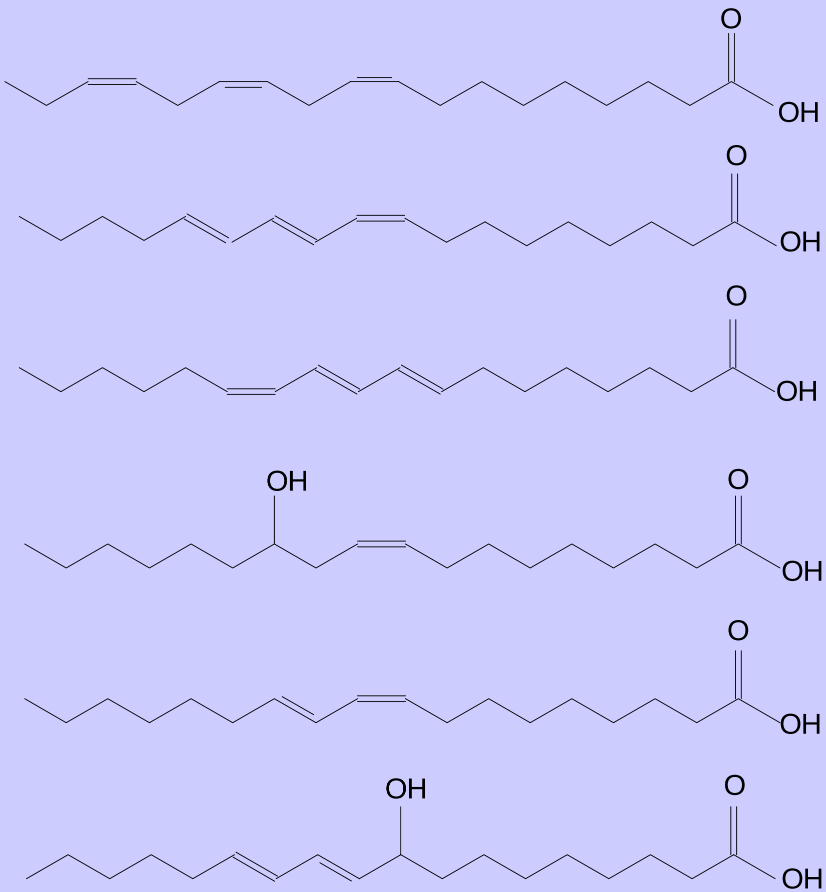
Introduction

Non-food research items related to oils and fatty acids at A&F

- Binders:
  - high-solid alkyd resins
  - alkyd emulsions
  - latex systems based on polyhydroxy alkanoates
  - paper coatings; sizing agents
  - emission free floor coverings
  - powder coatings based on renewable monomers
- Additives:
  - alternative cross-linkers for powder coatings
  - cobalt free drying catalysts
  - phthalate free plasticisers
  - surface active agents
- Solvents:
  - reactive diluents
- Biolubricants
- Pheromones

Introduction

Structural formula of functionalised fatty acids present in oils



alpha-linolenic acid

elaeostearic acid

calendic acid

ricinoleic acid

dehydrated ricinoleic acid

dimorphecolic acid

Codlemone from dimorphecolic acid

Hydroxy fatty acids; dimorphecolic acid

Dimorphoteca Pluvialis offers potential for new non-food products

Agronomical aspects have been evaluated in framework Dutch National Programme and European Programmes

Seeds of Dimorphoteca Pluvialis contain 12 % of oil from which dimorphecolic acid can be isolated

After isolation and purification chemistry has been explored;

Dimorphecolic acid can be epoxidised with good regioselectivity

Codlemone from dimorphecolic acid

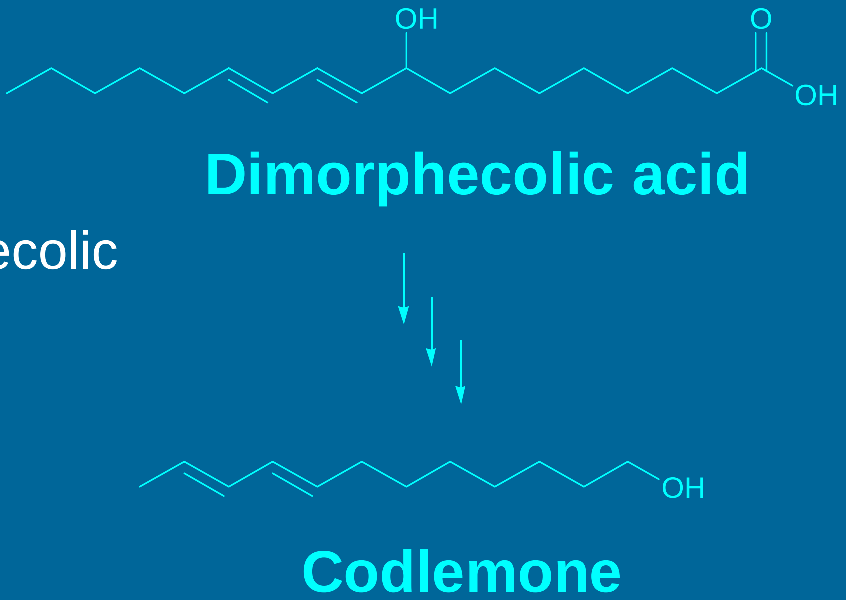
Synthesis of Codlemone

The codling moth causes damage to fruit production in orchards

Codlemone pheromone is produced by the female of the codling moth
Controlled release of the sex pheromone codlemone disrupts mating process of codling moths, decreasing its population

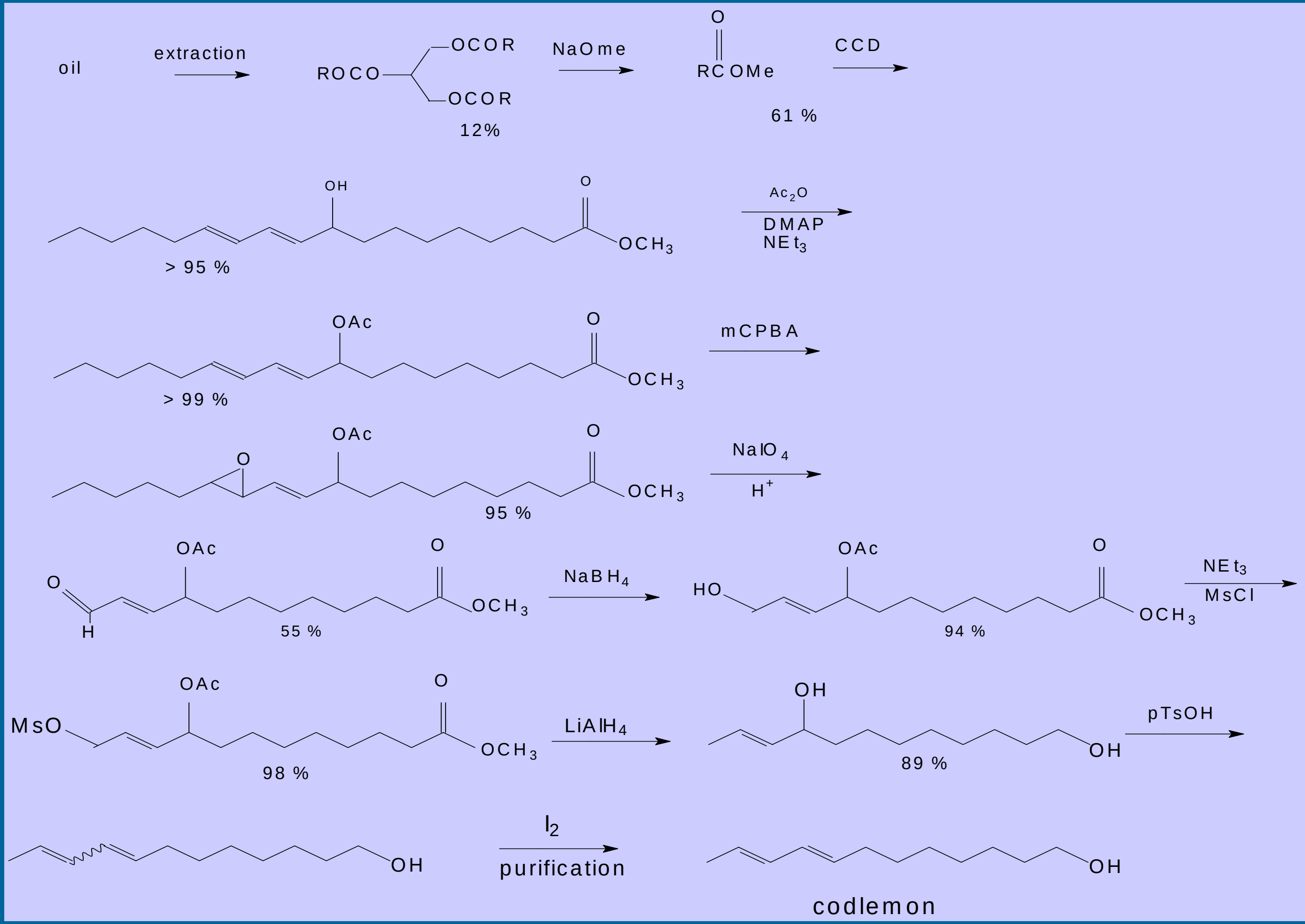
Synthesis of codlemone is a multi step synthesis leading to high prices

Regioselective epoxidation of Dimorphecolic acid offers potential for a new route to codlemone



Codlemone from dimorphecolic acid

Synthesis of pheromone



Two-component resin

- Based on commercially available materials
- Good flexibility
- Water resistant
- Base system is transparent, low in colour
- Potential alternative to PUR based systems
- Curing time:
  - ranges from 30 h at room temperature to <2 minutes at 150°C

Two-component resin

Properties

- Properties of thermosets based on triglyceride derivative A and (fatty acid based) hardener B. Samples (1 mm thick) were treated at 150°C for 15 minutes:

Hardener B	T_g [°C]	E-modulus [MPa]	Tensile strength [N/ mm^2]	Elongation at break [%]
B1	16	8	4.6	55
B1 + 1% kat.	20	10	9.1	43
B2	45	30	35	4
B3	–18	5	0.4	38
B4	11	9	4.4	63
B5	11	4	25	57

Renewable alkyd paints

World production of paint is approximately 26 million tonnes

Main components paint: pigments, solvents, binders, additives

Decorative sector is by far largest; over 60 % of volume

Decorative paints based on two types on main chemistries:

1) solvent borne alkyd paints
2) waterborne acrylic based paints

High solid alkyd resin based paints or waterborne alkyd emulsion paints offer potential for future

Renewable alkyd paints

Conventional alkyd paint:

• Solvent borne, main components organic solvent,binders, additives

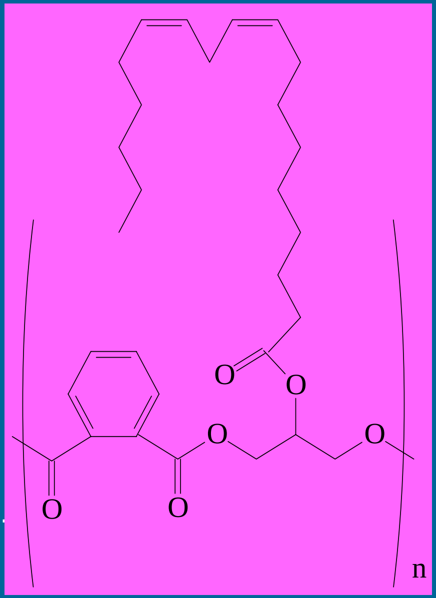
• oil: soya, safflower, sunflower, TOFA, etc.

• oil length: 35 - 85 (renewable)

• poly-alcohols: glycerol, (di)pentaerythritol, trimethylol propane, et

• poly-acids: (iso-, tere-, tetrahydro-)phthalic acid, trimellitic, etc

• modified alkyds: PU, silicone, amide, epoxy, vinyl etc



• Drying: Accelerated by cobalt based catalysts

Renewable alkyd paints

Objectives project in cooperation with paint producer SigmaKalon:

- To develop an air-drying high solids binder completely based on renewable raw materials with properties at least comparable to those of conventional alkyds

  Primary product properties

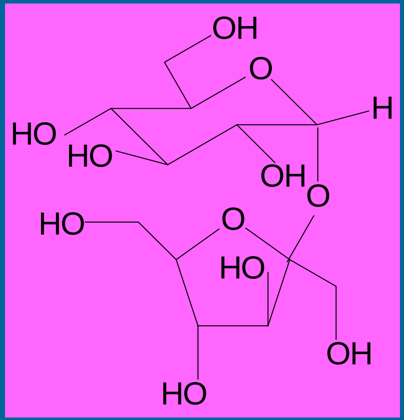
  - Viscosity < 40 dPa.s (Solids : $\geq$ 90 % ; T: 23 ^oC)
  - Good drying properties

- Reactive diluents based on renewable raw materials

Renewable alkyd paints

Sucrose-based alkyd resin

- Starting material: sucrose



Sucrose produced from sugar beet or sugar cane by many companies including Sensus (Neth.) and Orafti (Belgium)

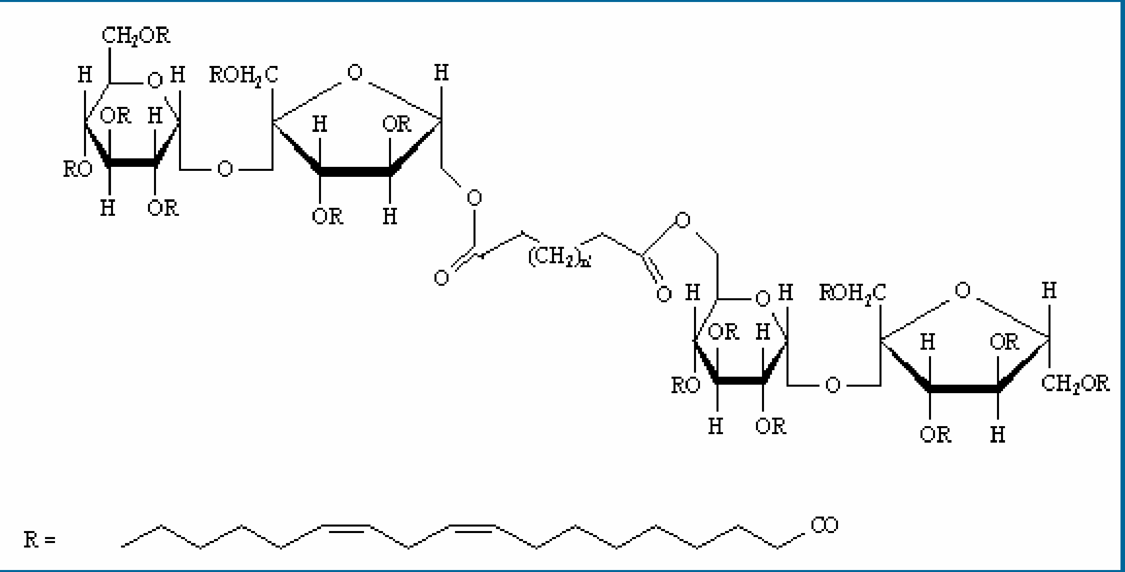
Current estimated production volume: 140 million tonnes/annum

Current estimated price: € 0.18/kg

Renewable alkyd paints

Sucrose-based alkyd resin

Oligomeric sucrose-linoleate binders:



Parameters varied: type of chain extender/ratio chain extender/FAME
additional acetylation
processing method; trans - or interesterification

Renewable alkyd paints

Sucrose-based alkyd resin

Formulations tested: opaque, white, gloss formulations

- 47 - 53% oligomeric sucrose binder
- 3 - 11% D40
- 1% dispersant
- 36% TiO_2
- 0.8% anti skinning agent
- 3.0 - 3.7% Ca
- 1.1 - 1.5% Zr
- 0.31 - 0.43% Co

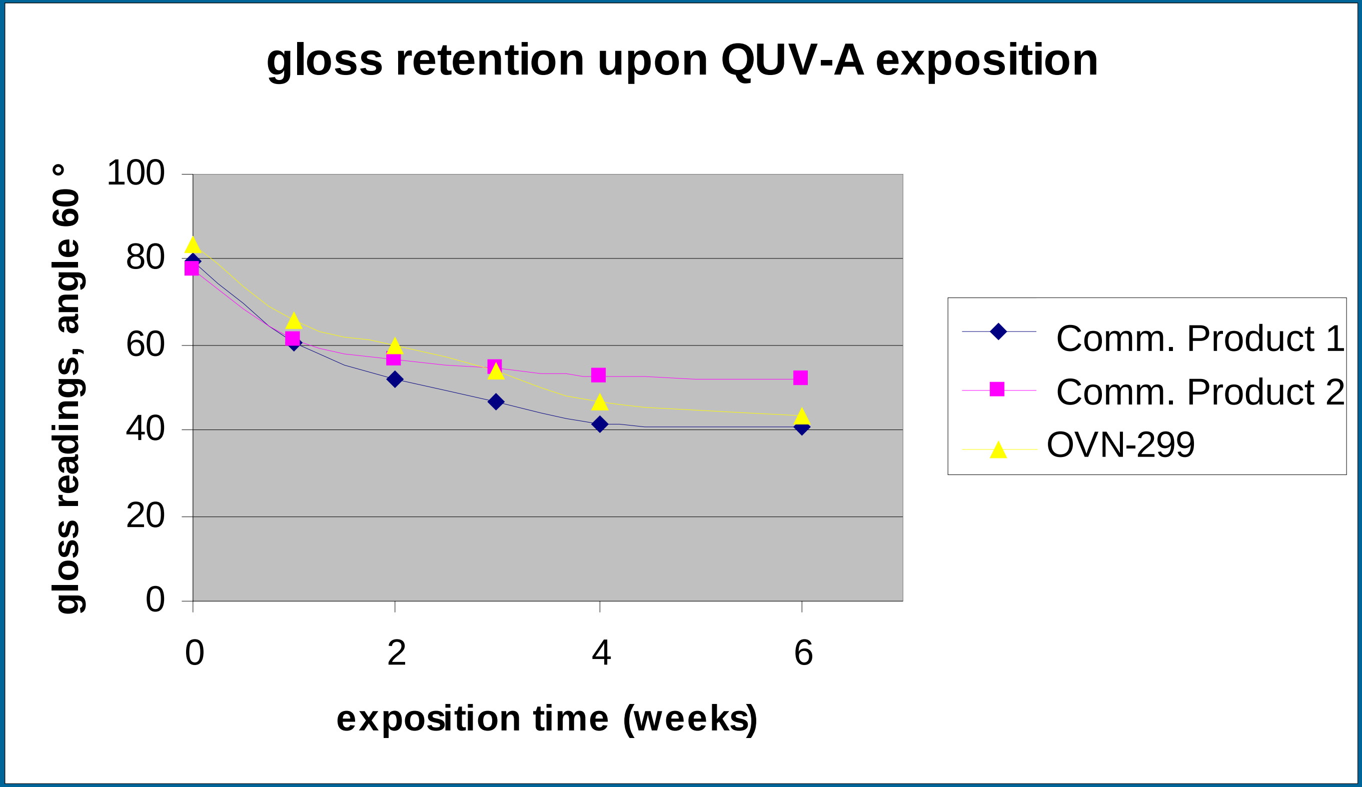
Renewable alkyd paints

Sucrose-based alkyd resin

Test	OVN-227	OVN-228	OVN-231	Comm. product
Low shear viscosity (dPa.s)	14.0	14.0	13.8	
High shear viscosity (dPa.s)	9.8	> 10	9.6	4.6
Solids (%)	89.6	93.7	85.7	80.5
VOC (g / L)	134	83	180	260
Whiteness	77.1	75.4	74.8	76.5
Drying (RT; 50 % RV)	0	0	0	0
Drying (5°C; 90 % RV)	0	0	0	0
Gloss	98.8	88.9	83.5	85.9
Water sensitivity (4 days)	0	0	0	0
Levelling	0 - 1	0 - 1	0 - 1	1 - 2
Hiding power	1	1	1	1

Renewable alkyd paints

Sucrose-based alkyd resin



Renewable alkyd paints

Sucrose-based alkyd resin

Main test results/Conclusions Sucrose based alkyd resins:

- low VOC-values 80 - 270 g/l
- fast (through) drying
- good initial whiteness
- hard, flexible films
- levelling is very good (due to high solids content)
- good gloss retention in QUV-A
- high shear viscosity

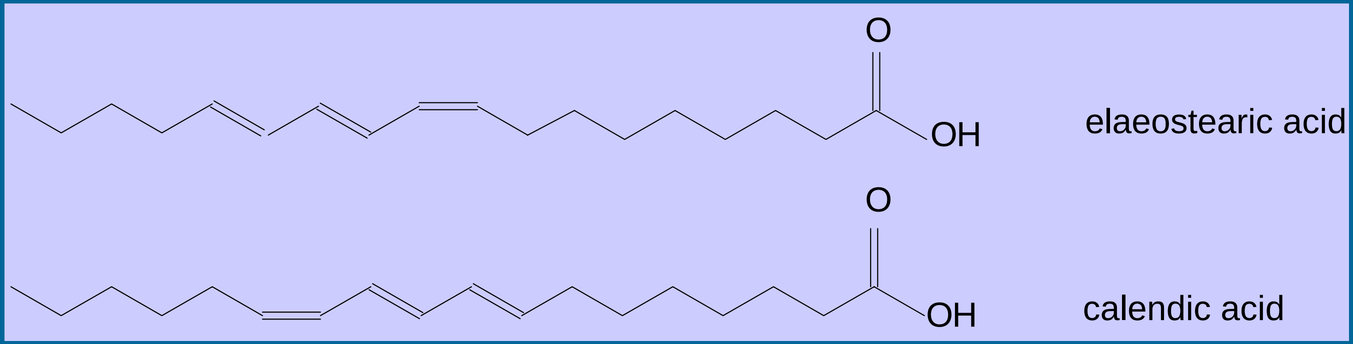
E.A. Oostveen, J. G.J. Weijnen, J. van Haveren, M. Gillard, Air drying paint compositions comprising carbohydrate based polyesters, WO 03064498

Renewable alkyd paints

Reactive diluents and resins from calendula oil

- Calendic acid offers potential to come to vegetable oil based paints with unique/improved drying characteristics

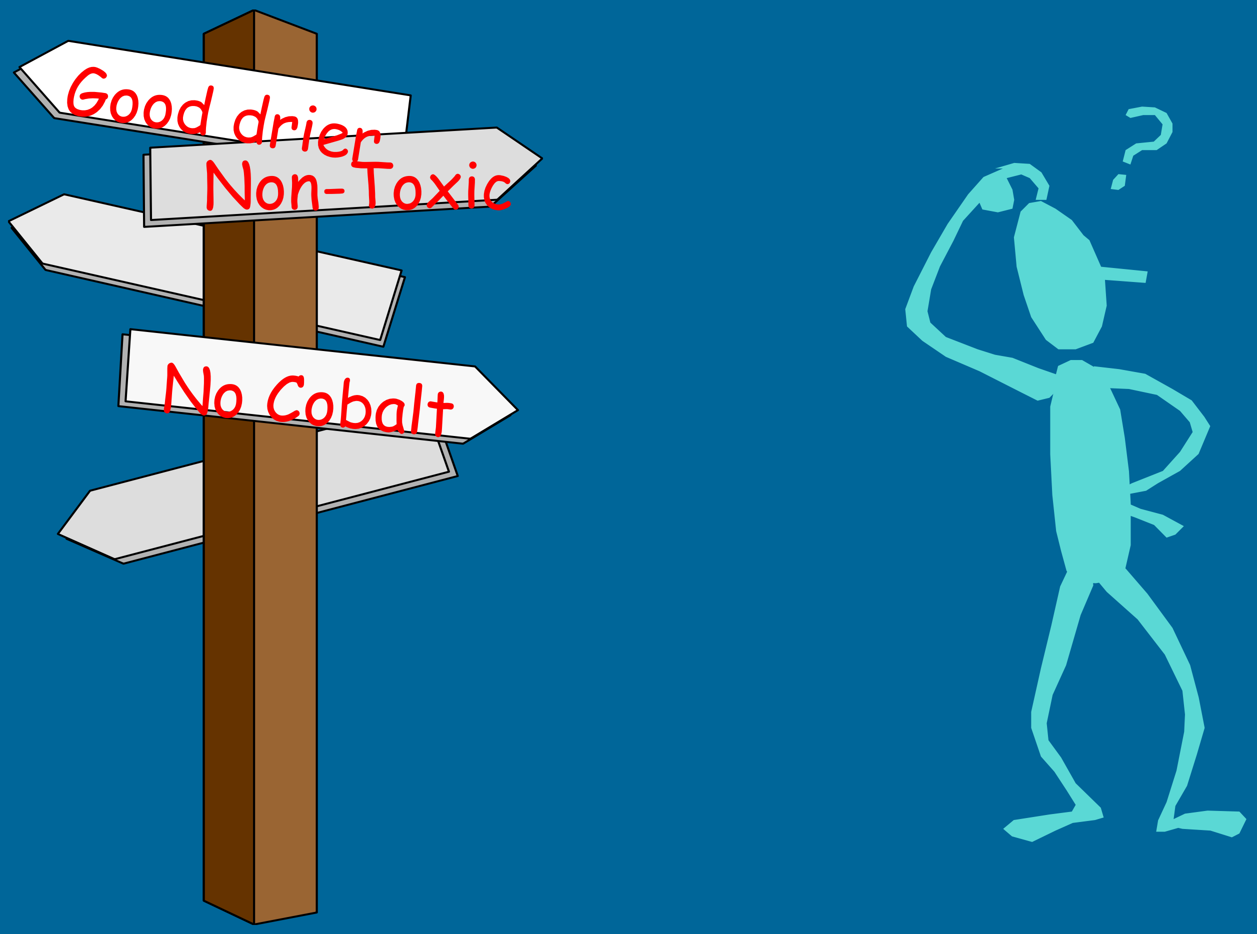
- Calendic acid is structurally related to the unsaturated fatty acid - eleaostearic acid- present in tung oil; calendula oil could be a (cheaper) alternative to tung oil



- Within WUR programme on improving agronomical aspects and exploration of paint properties of Calendula oil

Cobalt-free drying catalysts

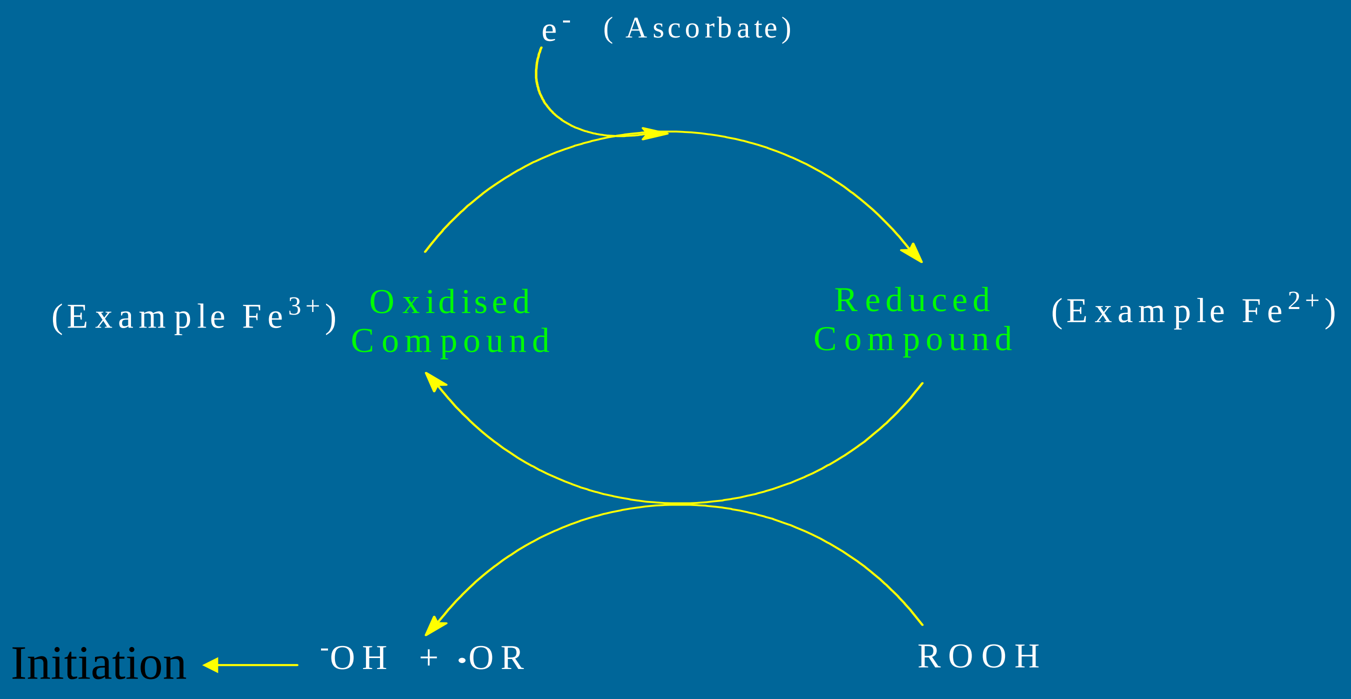
Cobalt free drying catalysts



Cobalt-free drying catalysts

Cobalt free drying catalysts

Biomimetic approach

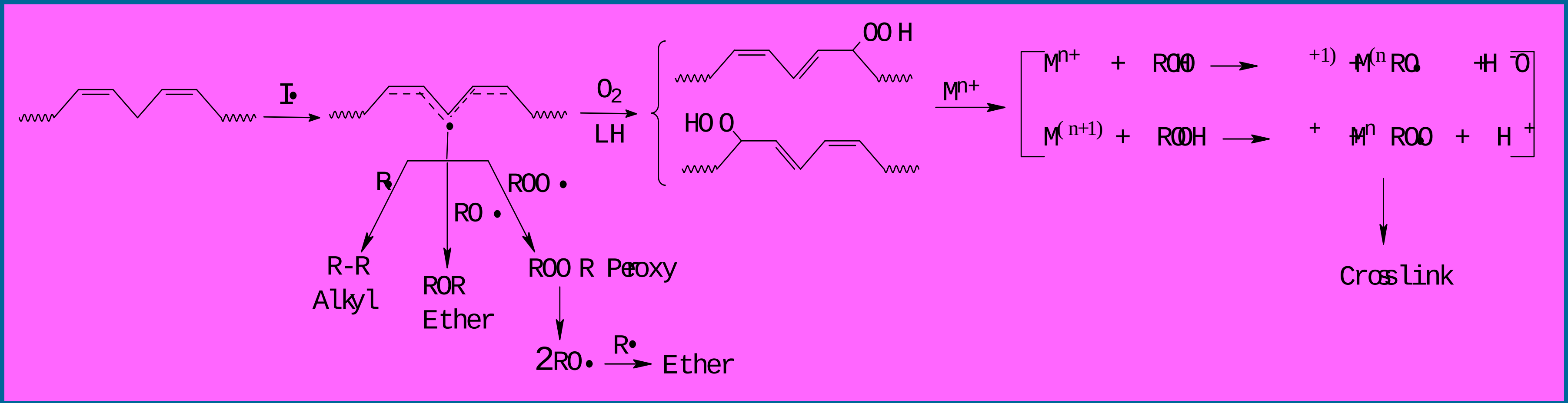


Cobalt-free drying catalysts

The oxidation and oligomerisation of neat ethyllinoleate

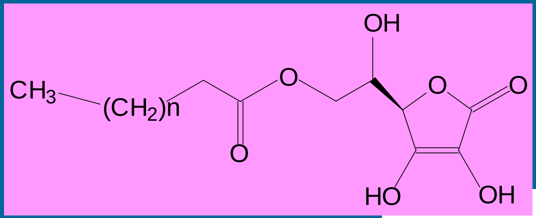
The oxidation and oligomerisation of ethyllinoleate was studied for the combination Fe/Ascorbylpalmitate at various ratio’s using NMR, FT-IR, SEC and Peroxide Value as techniques

Generally assumed reaction mechanism for metal ion catalysed oxidation of unsaturated fatty acids

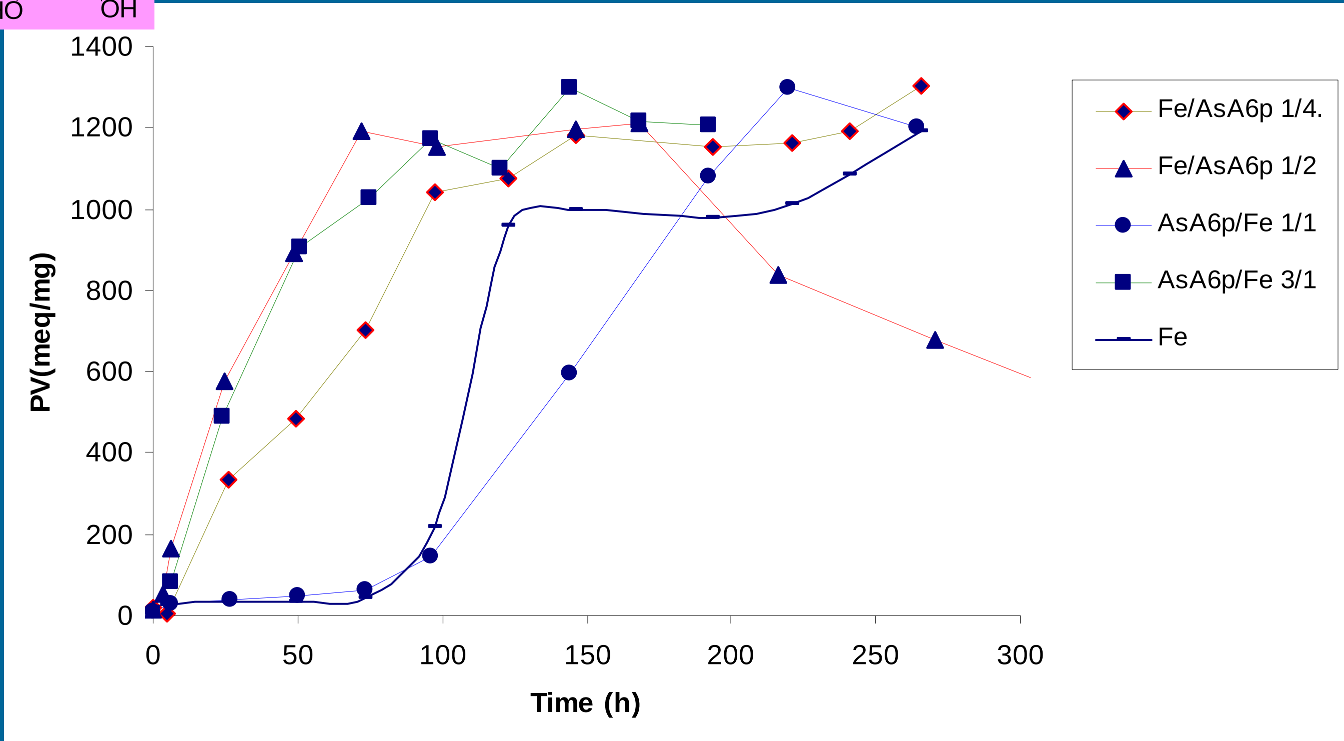


Cobalt-free drying catalysts

The oxidation and oligomerisation of neat ethyllinoleate



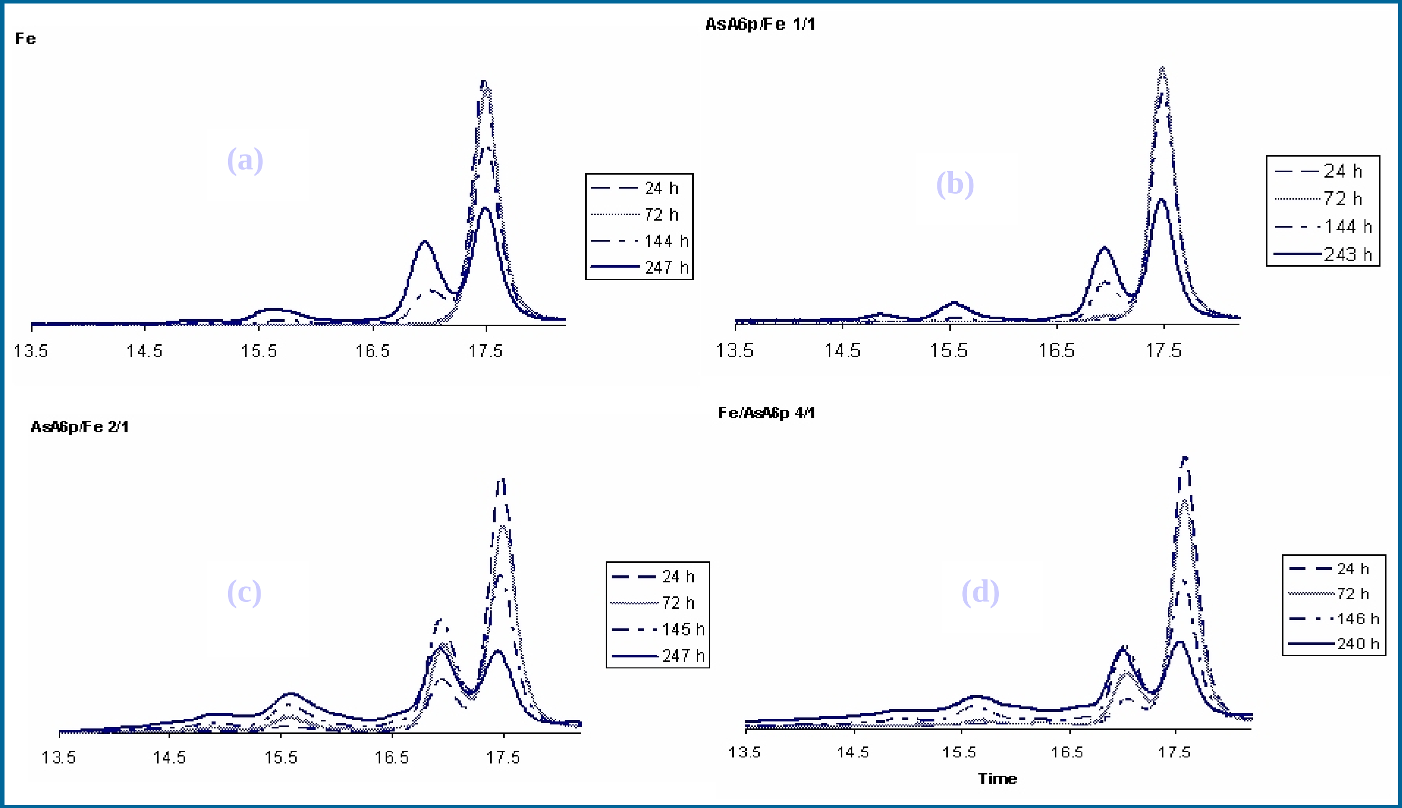
Hydroperoxide formation and decomposition



Cobalt-free drying catalysts

The oxidation and oligomerisation of neat ethyllinoleate

Size exclusion chromatography data



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Cobalt-free drying catalysts

The oxidation and oligomerisation of neat ethyllinoleate

Conclusions ethyllinoleate modelsystem:

- The system Fe/Ascorbylpalmitate is an effective catalyst towards the oxidation and oligo/polymerisation of ethyllinoleate

- Byproduct formation seems to be different (carboxylic acids) than for Co based catalysts (aldehydes) and potentially less

Ref:: *Oxidation and Oligomerization of Ethyl Linoleate under the Influence of the Combination of Ascorbic Acid 6-palmitate/Iron-2-ethylhexanoate*, Fabrizio Micciche; Jacco van Haveren, Eef Oostveen,. Weihua Ming,. Robert van der Linde

Accepted for publication in Applied Catalysis

Cobalt-free drying catalysts

Drying time recorder

Starting point

End point

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Cobalt-free drying catalysts

Drying times

High Gloss White Paint based on : Setal 16 LV WS-70

Drier	% of active drier	Incubation Time (days)	Dust free drying (h)	Tack-free drying (h)	Total drying time (h)	Hardness (s/K) 5 days	Skin formation	Whiteness Index
Fe/AsA6p 1/1	0.07 Fe	14	0.6	2.03	8.83	76.0	N.O.	80.2
Fe/AsA6p 1/2	0.07 Fe	14	0.66	1.76	9.96	69.4	O.	80.3
Fe/AsA6p 1/3	0.07 Fe	14	0.83	0.7	7.03	73.7	O.	80.1
Fe/AsA6p 1/4	0.07 Fe	14	2.1	0.9	6.63	68.1	O.	80.0
Co + Exkin 2	0.07 Co	14	3.3	4.23	14.1	73	N.O.	82.8
Mn	0.04 Mn	12	0.66	6	12.5	52	O.	83
Mn	0.07 Mn	12	0.66	4.76	9.9	51.3	O.	82.1

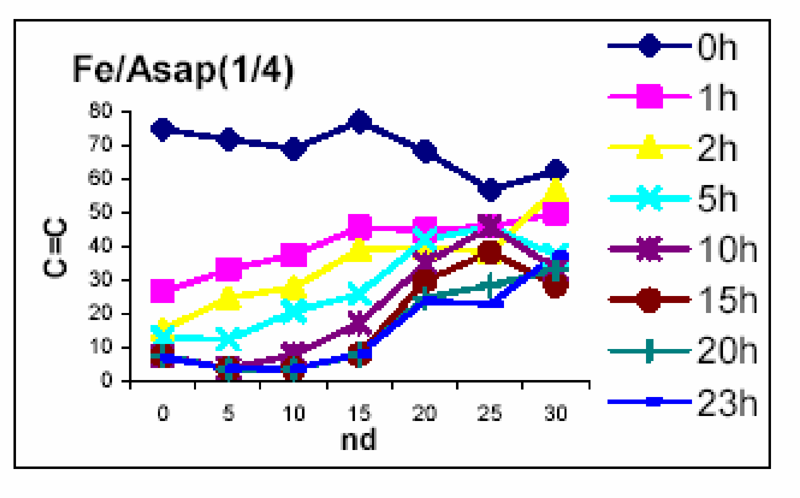
Drier	% of active drier	Incubation Time (days)	Dust free drying (h)	Tack-free drying (h)	Total drying time (h)	Hardness (s/K) 5 days	Skin formation	Whiteness Index
Fe/Im/AsA6p 1/4/1	0.07 Fe	18	0.7	2.66	4.5	73.6	N.O.	80.6
Fe/Im/AsA6p 1/4/2	0.07 Fe	18	0.63	0.43	2.2	80.6	O.	80.8
Fe/Im/AsA6p 1/4/3	0.07 Fe	18	0.6	1.53	5.8	85	O.	81.5
Fe/Im/AsA6p 1/4/4	0.07 Fe	18	1.16	1.53	6.6	80	N.O.	81.2
Co + Exkin 2	0.07 Co	12	3.3	4.23	14.1	73	N.O.	82.8
Mn	0.04 Mn	12	0.66	6	12.5	49	O.	83
Mn	0.07 Mn	12	0.66	4.76	9.9	51.3	O.	82.1

N.O. = not observed

O. = observed

Cobalt-free drying catalysts

Depth profile of film



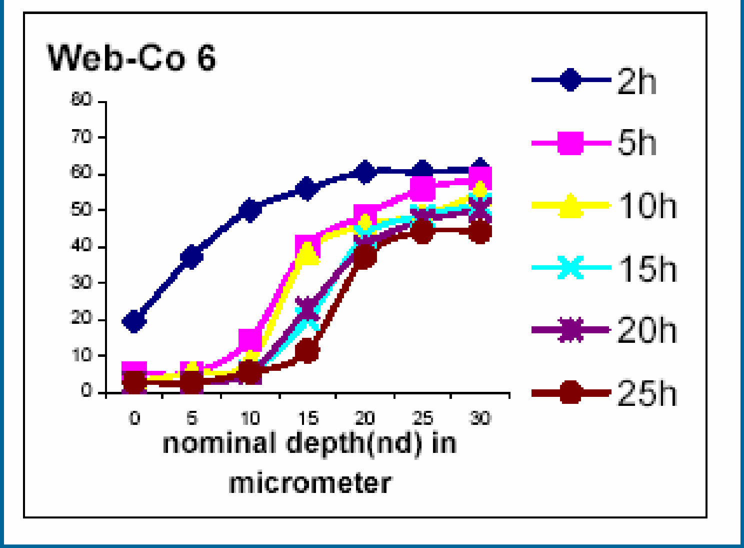


Figure : Intensity of C=C peaks versus thickness of short oil-based alkyd films determined by confocal Raman spectroscopy at 1 h time intervals

Cobalt-free drying catalysts

Conclusions

What did we achieve?

1. Non-Toxic
2. Drying time and film hardness comparable with Co
3. No color formation
4. Stable
5. No skin during storage
6. Economically attractive

E.A. Oostveen, F. Miccichè and J. van Haveren, R.v.d. Linde, “Drier for Air Drying Coatings”, W.O. 03 09 3384

General conclusions and outlook

- Functional fatty acids are versatile building blocks for many products and applications

- Although oleochemistry is well-established field, there are still plenty of opportunities for innovative technologies and new raw materials

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