TALL OIL FATTY ACIDS

100% biobased building block for Alkyd Emulsions

Presented by: Patrick Van Waes

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Agenda

- Pine Chemicals: Recap
- Tall Oil Fatty Acids: Introduction
- Alkyd Emulsion preparation
- Performance in waterborne alkyd emulsion based paint
- 100% Biobased Sustainable Solution
- Conclusions

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Pine Chemicals: Efficient Use of Natural Resources

Pine Chemical Bio-Refinery Overview

Crude Tall Oil (CTO) →

Crude Tall Oil Fractions

- Palmitic Heads
- Tall Oil Fatty Acids (TOFA)
- Distilled Tall Oil (DTO)
- Rosin Acids (TOR)
- Tall Oil Pitch

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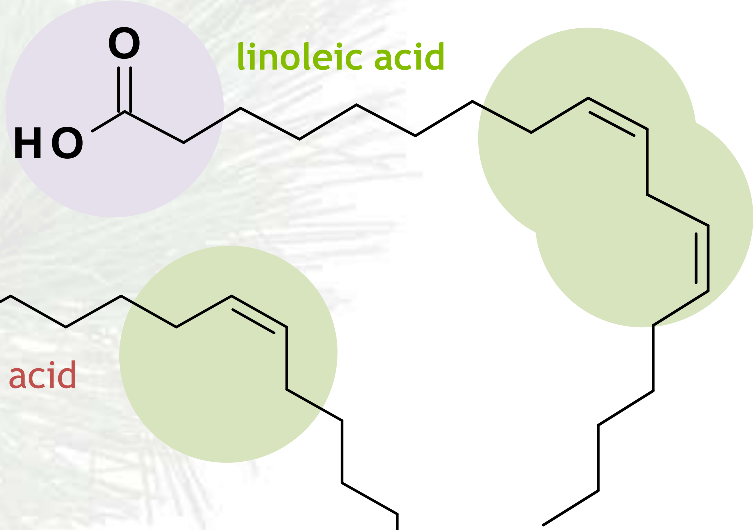
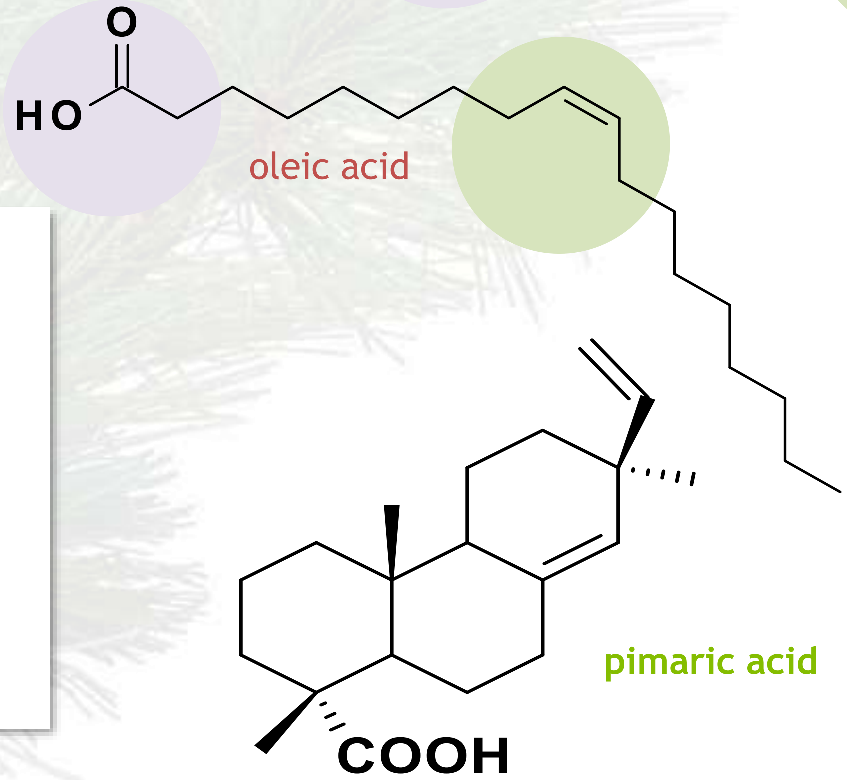
What are Tall Oil Fatty Acids ?

Carboxyl Group
("acidity")
Measured by acid value





Double Bonds
("unsaturation")
Measured by iodine value

Reactions of Carboxyl Groups:

- **Soap Formation**
  Greases, Emulsifiers
- **Esterification**
  Lubricants, ALKYDS, Epoxies
- **Alkoxylation**
  Detergents
- **Imidazolines**
  Corrosion Inhibitors, Coatings

Reactions of Double Bonds:

- **Oxidation**
  Drying Oils
- **Sulfonation**
- **Cycloaddition**
  Dimer Acids
- **Maleic Anhydride Adduction**
  Plasticizers

Tall Oil Fatty Acids: Composition and Features

	FA-2	FA-1	F-2
Acid Value, mg KOH/g	196	194	196
Fatty Acids, %	98.0	93.8	96.0
Rosin Acids, %	0.9	2.5	1.6
Unsaponifiables, %	1.3	2.0	1.0
Color, Gardner	3.0	4.5	4.1
$C_{18:1}$ (oleic acid types)	50.2	42.5	31.5
$C_{18:2}$ (non-conj. linoleics)	35.5	29.8	42.7
$C_{18:2}$ (conjugated linoleics)	4.6	8.7	7.3
$C_{18:3}$ (linolenic acids)	2.8	2.5	10.2
Saturated fatty acids	4.0	5.7	2.5
Other fatty acids	1.5	5.7	5.1
Neutrals and non-eluting	0.5	2.6	-0.7

FA1

F-2

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Raw materials used

- Synthesis of medium oil waterborne alkyds with following alternative oils/fatty acids

Oil/fatty acids for raw alkyd				
Identification	**Oil/fatty acids type**	**Supplier**	**Iodine value**	**Acid value**
FA-2	TOFA	Kraton	130	195
F-2	TOFA	Kraton	156	194
F-2bis	TOFA	Kraton	153	193
SBO	Soybean oil	Kraton	131	201
FA-1	TOFA	Kraton	132	193
SFFA	Sunflower oil FA	Kraton	144	201

Other compounds for water emulsions		
Name	**Identification**	**Supplier**
KOH solution	/	Spolchemie
Maxemul 7201 anionic surfactant	/	Croda
Maxemul 7101 nonionic surfactant	/	Croda

Other compounds for raw alkyds		
Name	**Identification**	**Supplier**
Penthaerythritol	PENTA	Perstorp
Benzoic acid	BA	OQEMA
Phthalic anhydride	PA	Lida

Formulation of base medium oil alkyd

- Standard medium oil alkyd with 50% oil length and ∆OH = 50 mg KOH/g, conversion is limited to acid value around 7±1.5 mg KOH/g (in 100% dry matter)

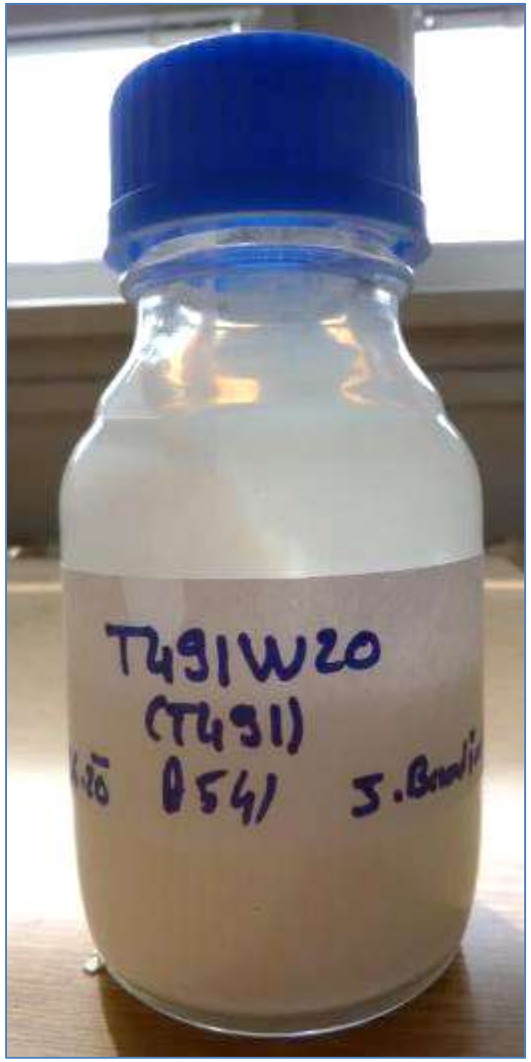
FA-2						
Compound	**Mass (g)**	**E (g/eq)**	**ea (eq)**	**eb (eq)**	**F**	**n0 (mol)**
TOFA	980,67	288	3,4051		1	3,4051
Penthaerythritol	496,63	74,0	6,7112		2	3,3556
Benzoic acid	245,63	122,0	2,0134		1	2,0134
Phthalic anhydride	485,00	34,8		13,9568	4	3,4892
∑	2207,93		12,1297	13,9568		12,2633
Constants						
Reaction H_20	157,93					
Theoretical yield	2050,00					
Alkyd constant	1,0110					
Excess of hydroxyl groups	1,151					
Oil length	0,50					
∆OH (mgKOH/g)	50,0					

- Ratios between benzoic acid/phthalic anhydride are kept constant ➔ the same amount of terminating compound

Emulsion formulation

Theoretical Formulation	
Compound	**Mass (g)**
Medium oil alkyd	500.00
Maxemul 7201 (nonionoc emulsifier)	20
Maxemul 7101 (anionic emulsifier)	20
50% sol KOH	3.2
Demi $H_2$0	500.00
∑	1043.2

Key parameters
Alkyd A.v (mg KOH/g)
8
Content KOH (%) in solution
50
Degree of Neutralization
40 %
Dry matter alkyd
Minimum 99 %
Maxemuls content
8.0 %
Temperature / viscosity during dispersion
Max 65° C/ Min 30 Pa.s



Emulsion procedure with dissolver

Procedure
1) Preheat Maxemul 7101(nonionic emulsifier) at 60 °C
2) Preheating of the alkyd at 80 °C, weight to the double wall vessel - minimal stirrer height – 20mm
3) While stirring (500 RPM) add 50 hm.% KOH solution, 1h homogenization
4) While stirring (500 RPM) add both Maxemuls, 30 min homogenization, maintain T<65 °C
5) Cool down to 55-60 °C, rapidly increase speed to 3500 RPM, add dropwise 2/3 of demineralized water (till inversion point). Water is preheated to 60 °C. After the inversion point the rest of water can be added more rapidly while increasing the stirrer height. At the end of water feed, rotational speed is slowly decreased to 1000 RPM
6) Cool down to 30 °C

Item	Key Parameter
Vessel	5L double wall, inner Ø = 155mm
Dissolver	Dispermat CN10-F2
Turbine stirrer	Ø= 65 mm
Height liquid	60 mm

Results

Preparation of waterborne emulsions – Improvement of technology

T49W14 –

Increase water feed time + increase Maxemuls content (10%) ➔ immediate phase separation

T49W24 – Change of stirrer (turbine) decrease of dispertion temperature ➔ slight phase separation after 24h

T491W23 – change of base alkyd same procedure as T49W24 ➔ slight phase separation after 72h

T491W20 – Dispersion with dissolver CN10-F2 ➔ **No phase separation, dilution test passed**

T49W23 – Dispersion with dissolver CN10-F2 ➔ slight phase separation after 72h

Stable emulsion obtained by decreasing the dispersion temperature and improving shear conditions by usage of a dissolver.

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Alkyd Emulsion Paint Formulation

Varnish

Compound	Amount (g)
Alkyd emulsion SFA2	79.9
Byk 012[1]	0.89
Byk 348[5]	1.29
Additol VXW4940N[4] (1:1 with H_2O)	17.92
Total	100.00

Pigmented formulation

Compound	Amount (g)
Water	13.45
Byk 012[1]	0.44
AMP 90[2]	-
Disperbyk 190[3]	1.43
TiO2 CR 510	21.06
Alkyd emulsion SFA2	48.94
Additol VXW4940N[4] (1:1 with H_2O)	9.35
Byk 348[5]	0.62
Rheolate solution[6]	4.71
Total	100.00

(1) Defoamer
(2) Co-dispersant and neutralizer
(3) Wetting and dispersing additive
(4) Drier
(5) Surfactant
(6) Thickeners (Rheolate 255: Rheolate 278: Dowanol DPM: H_2O 2:2:1:3)

Hardness Testresults

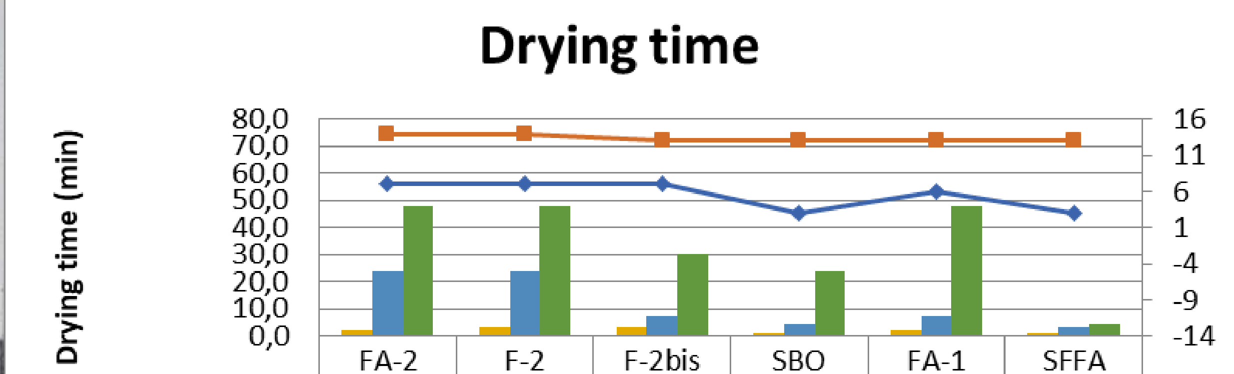
TiO2 only Pigmented paint formulation

	FA-2	F-2	F-2bis	SBO	FA-1	SFFA
After 1 day (%)	7.9	14.5	18.9	12.6	10.5	16.1
After 7 days (%)	28.7	36.4	42.2	27.5	22.6	23.3
After 14 days (%)	36.6	44.3	47.8	27.0	29.4	37.1
After 28 days (%)	41.8	48.5	52.9	35.2	32.2	38.9

- TOFA F-2 and TOFA F-2 bis both with higher amount of double bonds (iodine value) compared to the other products tested develop approximately 25 to 30% higher hardness in the final paint compared to Soyabean Oil and Sunflower Fatty Acid samples after 28 days

Drying Time Testresults:

TiO2 only pigmented paint formulation



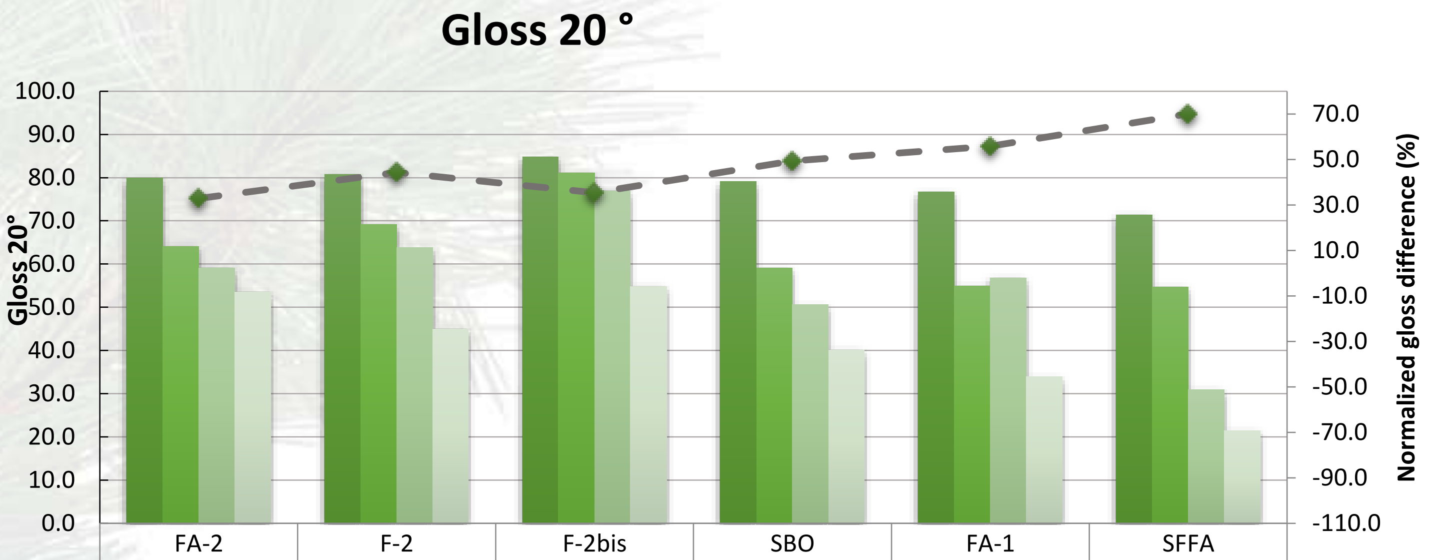
	FA-2	F-2	F-2bis	SBO	FA-1	SFFA
Degree I (h)	1,9	3,2	3,3	1,2	2,0	0,7
Degree II (h)	24,0	24,0	7,0	4,7	7,0	3,0
Degree III (h)	48,0	48,0	30,0	24,0	48,0	4,5
Degree IV (d)	7	7	7	3	6	3
Degree V (d)	14	14	13	13	13	13

- Goal was to achieve within 4 hours drying stage 1. Essential to dust particles which wouldn’t stick in the paint film.
- Further through drying will enhance the hardness and will take longer in general with higher double bonds containing TOFA

Note: Modified Bandow-Wolff test ISO-9117-5. First drying steps (I, II, III) are mostly driven by particle coalescence. ISO-9117-5 can be considered as sort of stickiness test

Gloss and Gloss Retention During Daylight exposurs

TiO2 only pigmented paint formulation

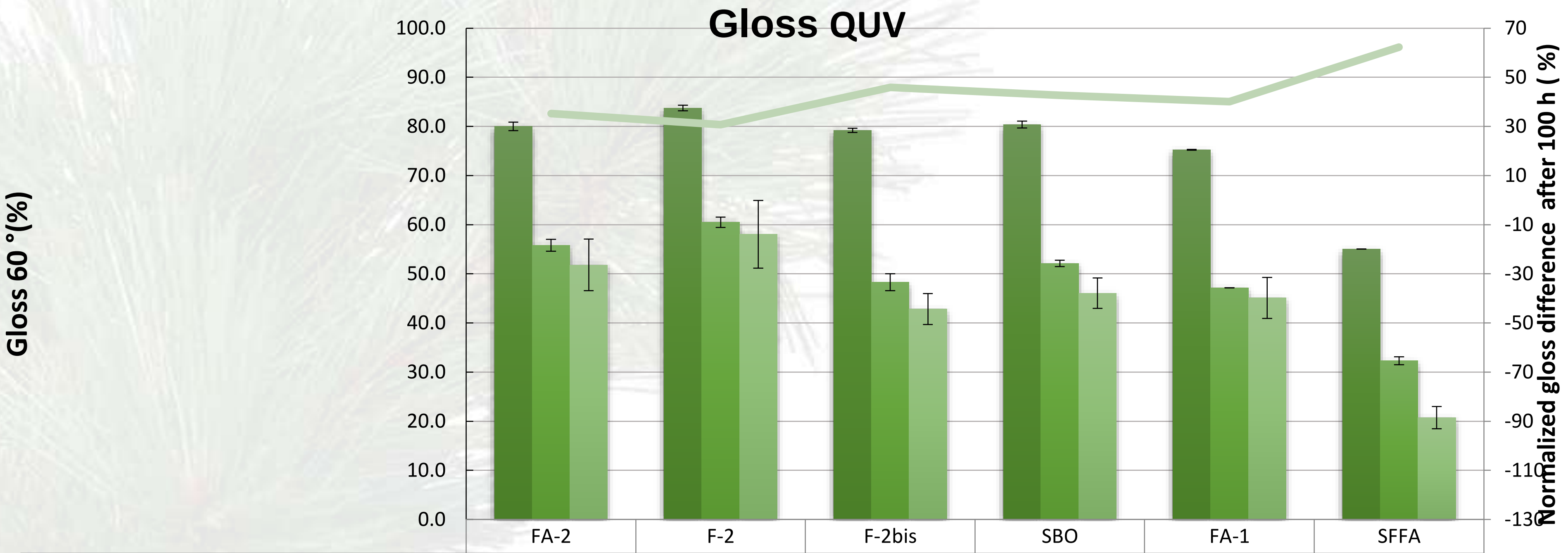


	FA-2	F-2	F-2bis	SBO	FA-1	SFFA
After 1 day Gloss 20° (%)	79.9	80.8	84.8	79.1	76.7	71.4
After 7 days (%) Gloss 20° (%)	64.1	69.2	81.1	59.1	54.9	54.7
After 14 days (%) Gloss 20° (%)	59.1	63.8	76.9	50.6	56.8	30.9
After 28 days (%) Gloss 20° (%)	53.6	45.0	54.8	40.1	33.9	21.4
Normalized gloss difference (%)	32.9	44.3	35.4	49.3	55.8	70.0

- FA-2, F-2bis and F-2 show high initial gloss combined with best gloss retention in daylight

Gloss and QUV Exposed Gloss Retention

Varnish only



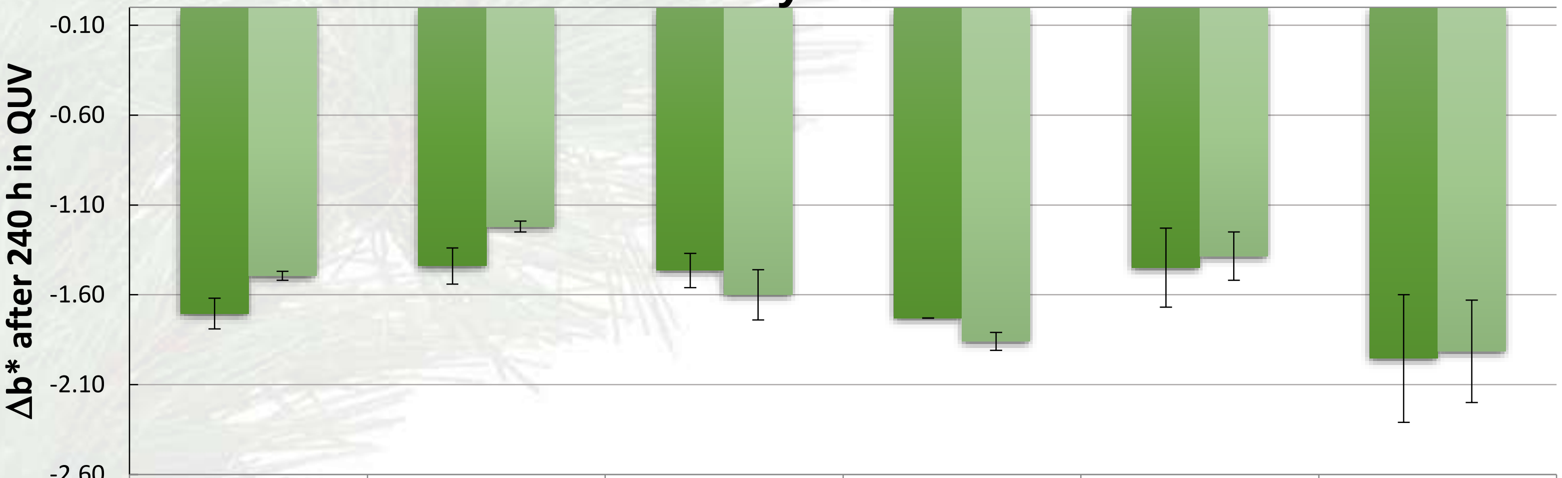
	FA-2	F-2	F-2bis	SBO	FA-1	SFFA
Before exposure Gloss 60 °/Average	80.0	83.8	79.2	80.4	75.3	55.1
100h Gloss 60 °/Average	55.8	60.5	48.3	52.1	47.2	32.3
500h Gloss 60 °/Average	51.8	58.1	42.9	46.1	45.1	20.8
Normalized gloss difference after 500 h (%)	35	31	46	43	40	62

- F-2 TOFA shows high initial gloss combined with best gloss retention.

Color and QUV exposure color change Testresults

TiO2 only Pigmented alkyd emulsion paint formulation

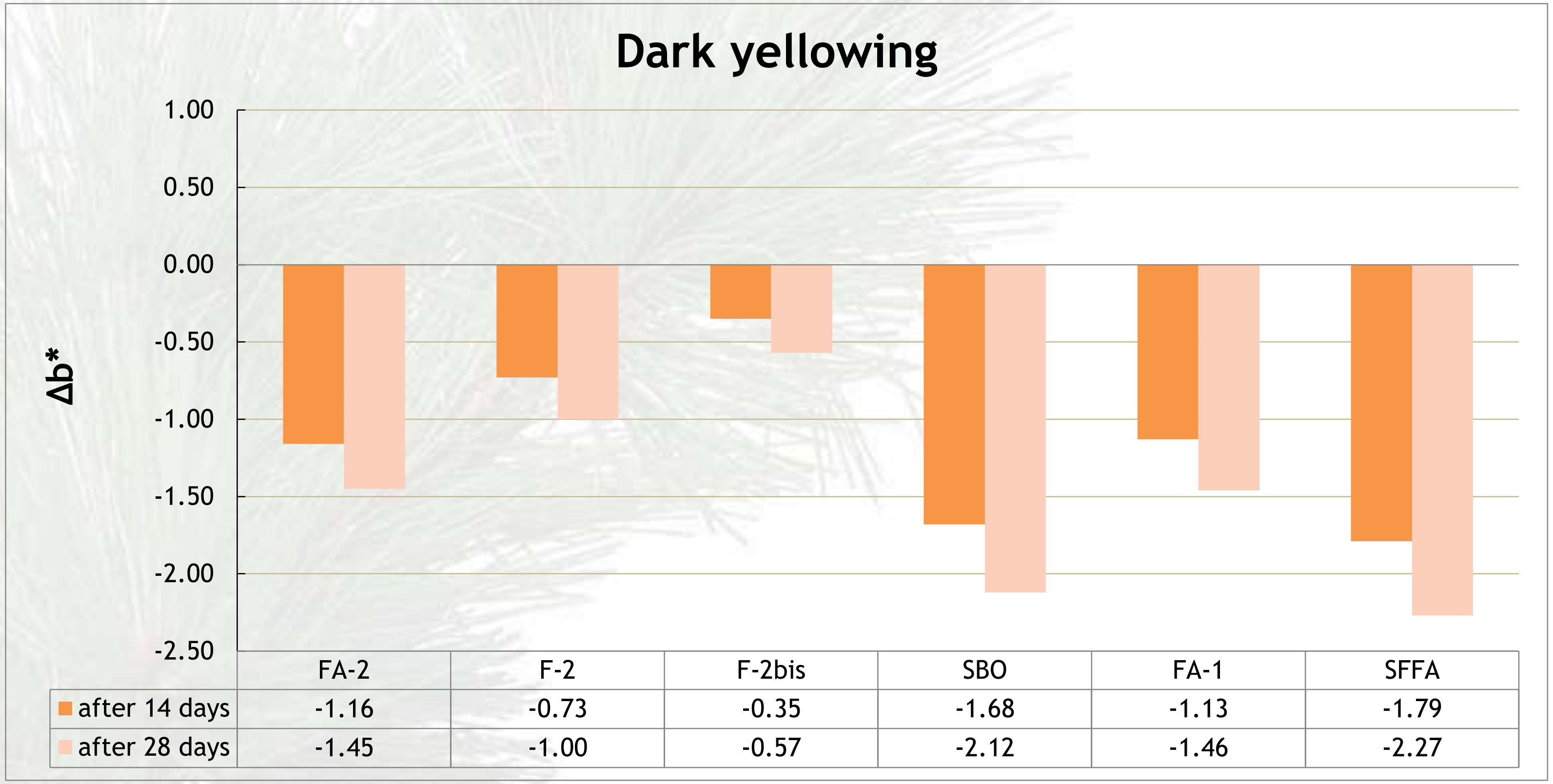
UV stability 500h



	FA-2	F-2	F-2bis	SBO	FA-1	SFFA
100h Δb*/Average	-1.71	-1.44	-1.47	-1.73	-1.45	-1.96
500h Δb*/Average	-1.50	-1.22	-1.60	-1.86	-1.39	-1.92

- F-2 and FA-1 TOFA have the smallest Δb* but differences are relative smaller with TOFA better performing compared to SBO and SFFA
- QUV testing was finished after 500 hours exposition (similar trend as after 240h)

Dark Yellowing:



	FA-2	F-2	F-2bis	SBO	FA-1	SFFA
after 14 days	-1.16	-0.73	-0.35	-1.68	-1.13	-1.79
after 28 days	-1.45	-1.00	-0.57	-2.12	-1.46	-2.27

- Samples were kept for several weeks with no exposure to daylight to observe color changes linked with alkyd technology
- TOFA products showcase highest color stability with especially F-2 and F-2bis

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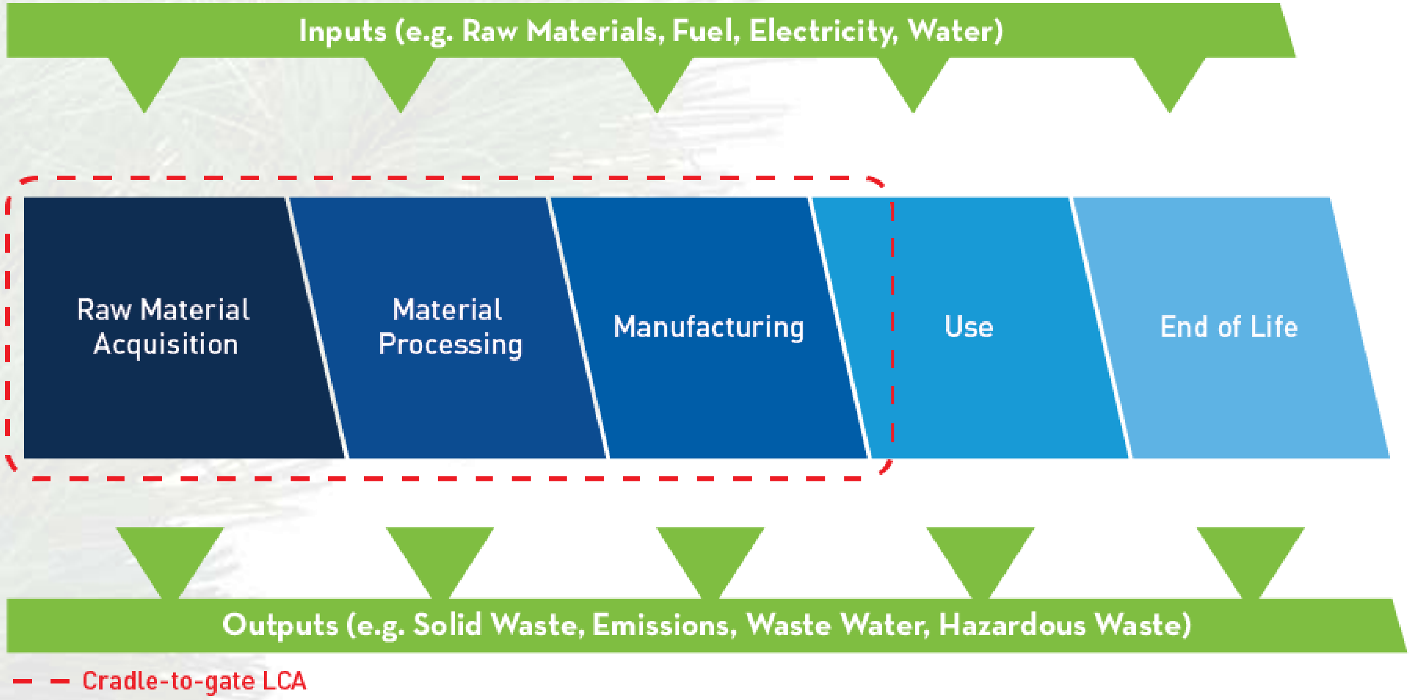
Tall Oil Fatty Acids: Sustainability Embedded From Nature

- 100% Biobased & Certified
- Sourced from Responsibly Managed Forests
- Do Not Compete for Land with Food Crops
- Are Not Genetically Modified
- Do Not Require Land-Use Change

Life Cycle Assessment (LCA)

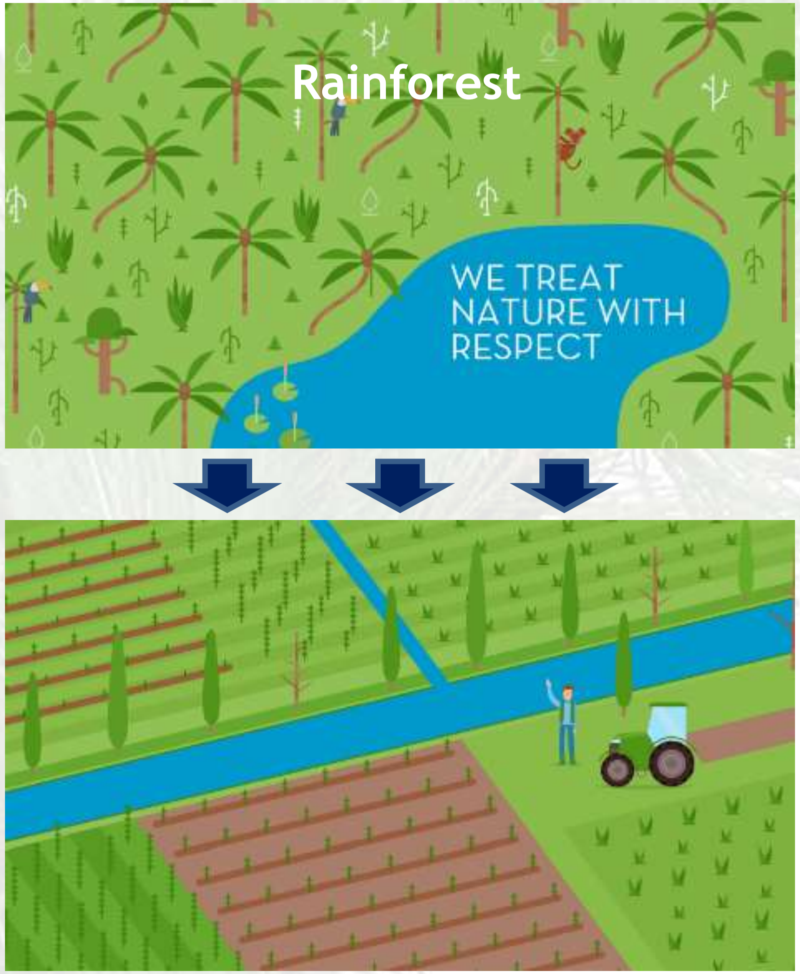
LCA is a methodology used to evaluate the environmental impacts associated with all the stages of a product or service's life.



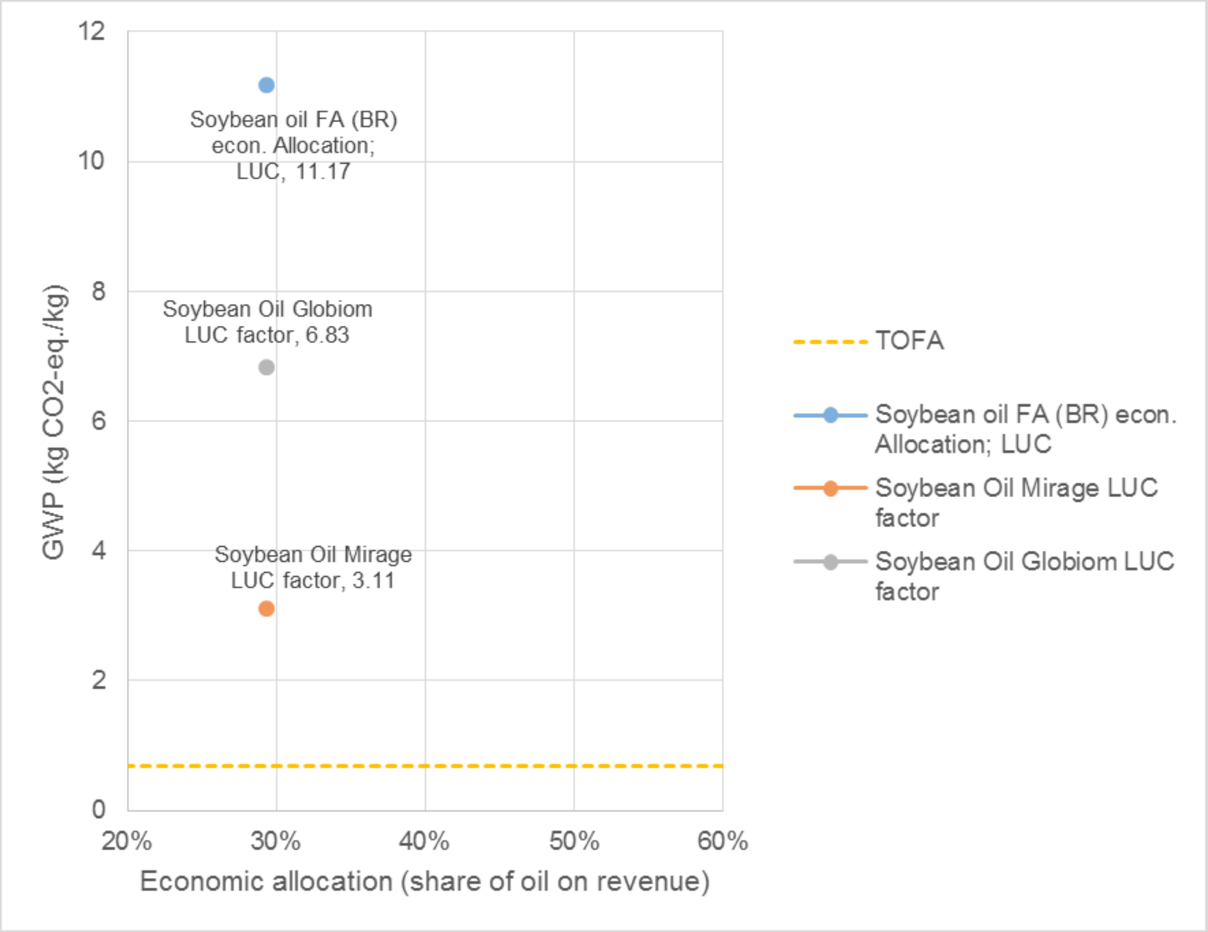
We Use LCAs:

- To provide transparency on our product's environmental impact
- As decision-making tool in raw material selection, transportation route
- As collaboration tool with suppliers, supply chain partners and customers

Minimal Land Use Change (LUC) with SYLFAT™ 2 TOFA



SYLFAT™2 TOFA CO2 eq / Kg is 0.69kg*
of which LUC contribution is negligible.



*LCA conducted by 3rd party. Excludes biogenic GWP

SYLFAT™ 2 TOFA and LUC Carbon Footprint Impact

Replacing 1T of SOFA* resin by TOFA produced in our Nordics facilities results in **10T of CO_2 eq. reduction.**

SOFA from Brazil @ 11.2 Kg CO_2 eq/Kg
SYLFAT™ 2 TOFA @ 0.7 Kg CO_2 eq/kg

Replacing 1000 T of SOFA* resin by TOFA produced in our Nordics facilities **corresponds to 10500T CO_2 eq. reduction :**

- **19772 Route 66 Harley Davidson Road Trips**
  - *1 trip is equivalent to 0.53 Mt CO_2*
- **12185 Round Trips Brussels - New York**
  - *1 seat is equivalent to 0.86 Mt CO_2*

**SOFA: Soyabean oil fatty acid*
This comparison excludes biogenic GWP component

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Conclusions

Tall Oil Fatty Acids allow the production of stable alkyd emulsions for high quality waterborne paints

- Which exhibit very good surface properties in TiO_2 pigmented systems.
  - *High hardness*
  - *High initial gloss en good gloss retention*
  - *Good color stability*
- Which embed a very high concentration of bio-based feedstock from sustainable origin
- Which allow a substantial reduction of the carbon footprint from raw materials

Questions?

Patrick Van Waes

Market Development Manager, Kraton

Chemical engineer with 32 years of coatings experience in multiple functions. More than five years with Kraton as a Market Development Manager with focus on the coatings industry.

Previously with AKZO Nobel and DuPont Titanium Technologies with a primary focus on architectural coatings.

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