Formulating for Stability and Long Shelf-Life

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Ontario SCC Education Day

September 18, 2018

Formulating for stability and long shelf life

Content

- Natural emollients
  - Properties, challenges and possibilities
- How to increase stability and keep functionality in natural formulations
- The do’s and don’ts

Rising demand for natural derived emollients

- Creates challenges for formulators since consumers certainly do not want to
  - Compromise on aesthetic experience
    - visual and sensorial
  - Sacrifice desired functionality on skin
    - moisturising, softening and caring
  - Pay more for “less” (in terms of perceived quality)

How much oil are we actually talking about?

- The use of natural oils in cosmetics

Applications with natural focus	% of oil typically used
Face Oil	up to 100
Body Oil	± 50
Massage Oil	± 50
Lipstick / lipbutter	30-50
Hair oil treatment	±50
Emulsion	10 to 20

And what kind of oils?

Unsaturated oils are often used as the main natural oil!

Name	**Sweet Almond Oil** *Prunus Amygdalus Dulcis Oil*	**Soybean Oil** *Glycine Soja Oil*	**Sunflower Oil** *Helianthus Annuus Seed Oil*	**HO Sunflower Oil** *Helianthus Annuus Hybrid Oil*
Typical FAC (%):				
Palmitic - C16:0	7	10	5	5
Stearic - C18:0	3	4	4	4
Oleic - C18:1	69	23	25	80
Linoleic - C18:2	**21**	**54**	**63**	7
Linolenic - C18:3	1	**8**	1	1
OSI (110°C)	12	6	6	20

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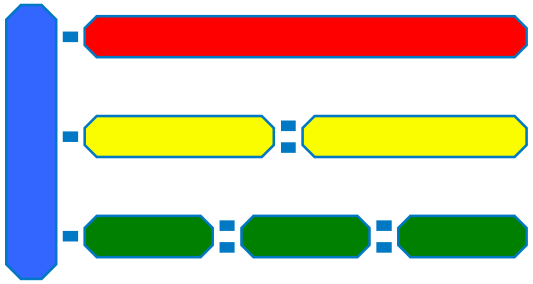
Formulating with emollients derived from plants creates challenges

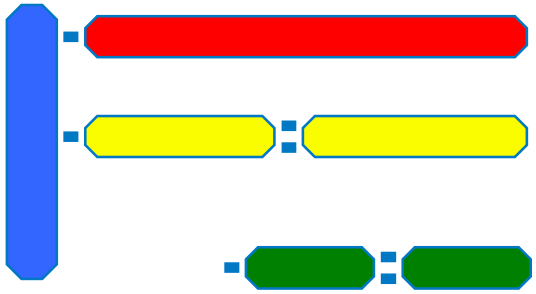
- Oxidative and hydrolytic stability of the base emollients of high importance
  - Mineral oils are usually stable against oxidation and hydrolysis
  - With emollients derived from plants;
    - oxidative stability depends on content of polyunsaturated fatty acids and quality
    - hydrolytic stability depends on strength of ester bonds and quality

Breakdown of fats – Hydrolysis (presence of water)



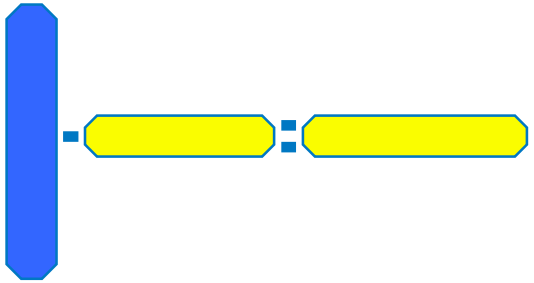
Triglyceride

+ water



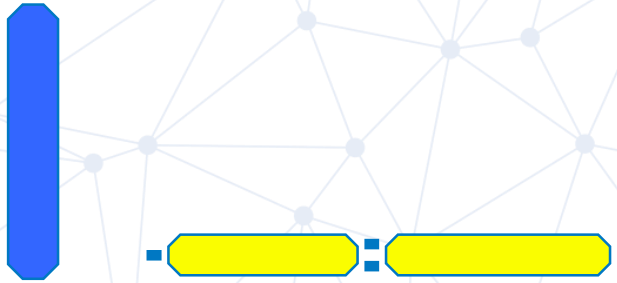
Diglyceride and free fatty acid

+ water



Monoglyceride

+ water



Glycerol

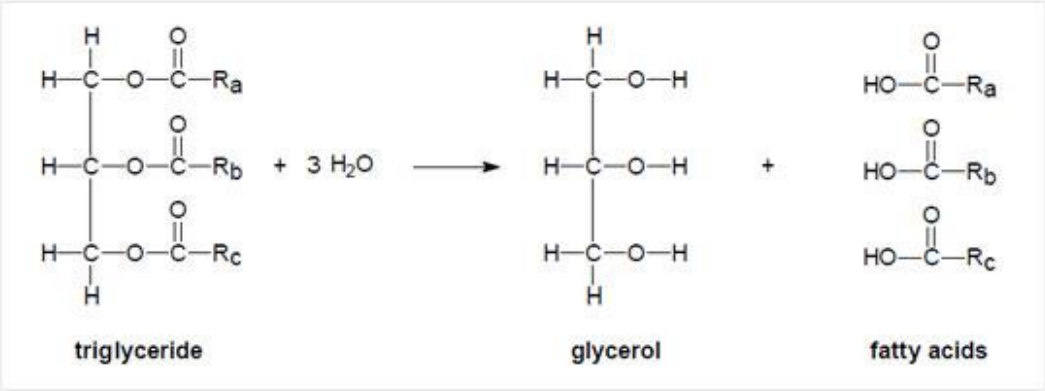
→ Changes in product consistency and stability

Challenge - pH

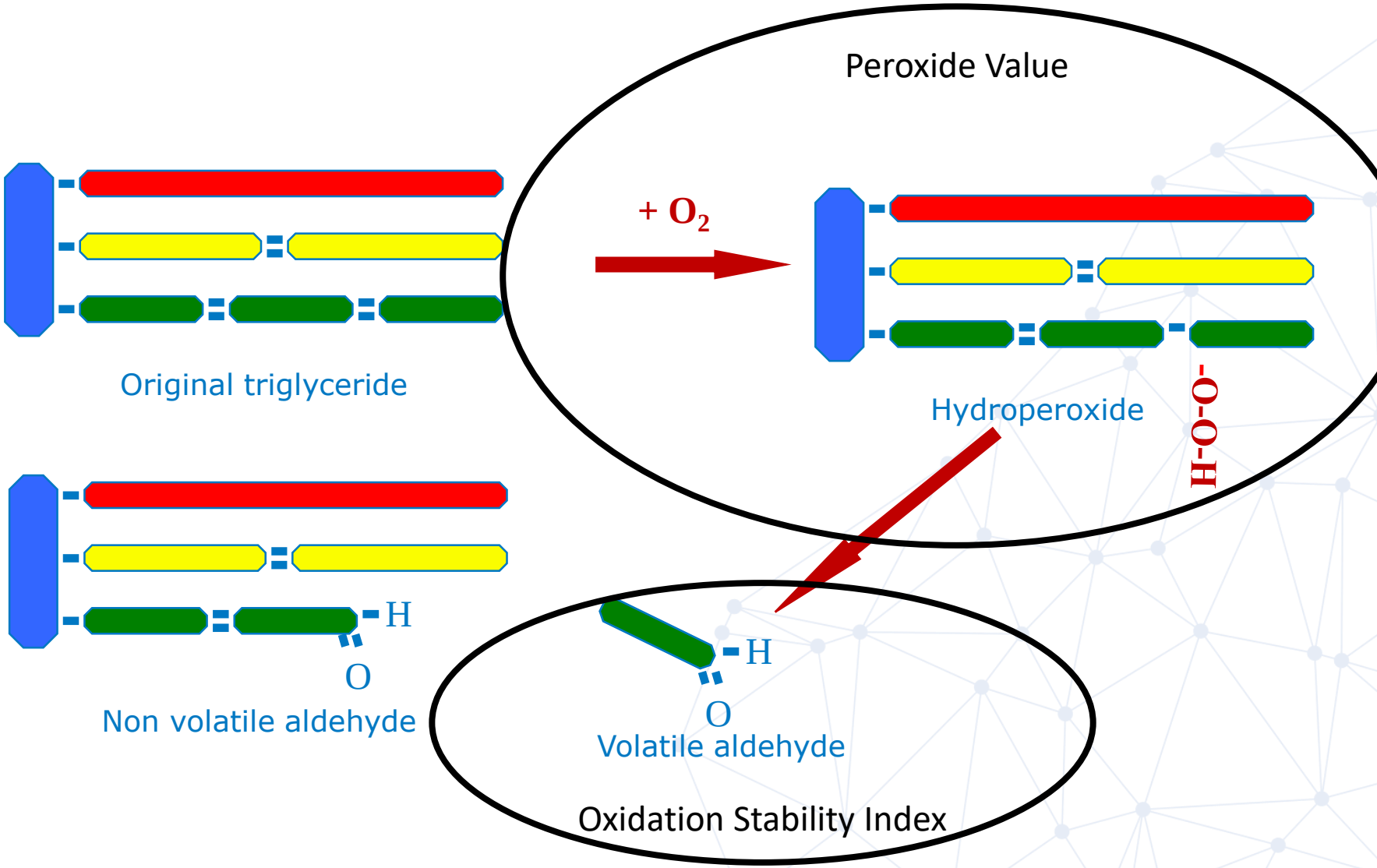
- Recommended pH range is given by the ester bond stability against hydrolysis
  - Valid for all esters and triglycerides
  - In general, stable in pH range 4 to 8
- Vegetable emollients are suitable for all purpose face care and body care applications
- Speciality applications like depilatory products (very low pH), hair straightening (very high pH) should not contain triglyceride or ester based emollients in direct base
- If allowed by application, the emollient can be added by the user (ie hair colouring)

Can hydrolysis be prevented?

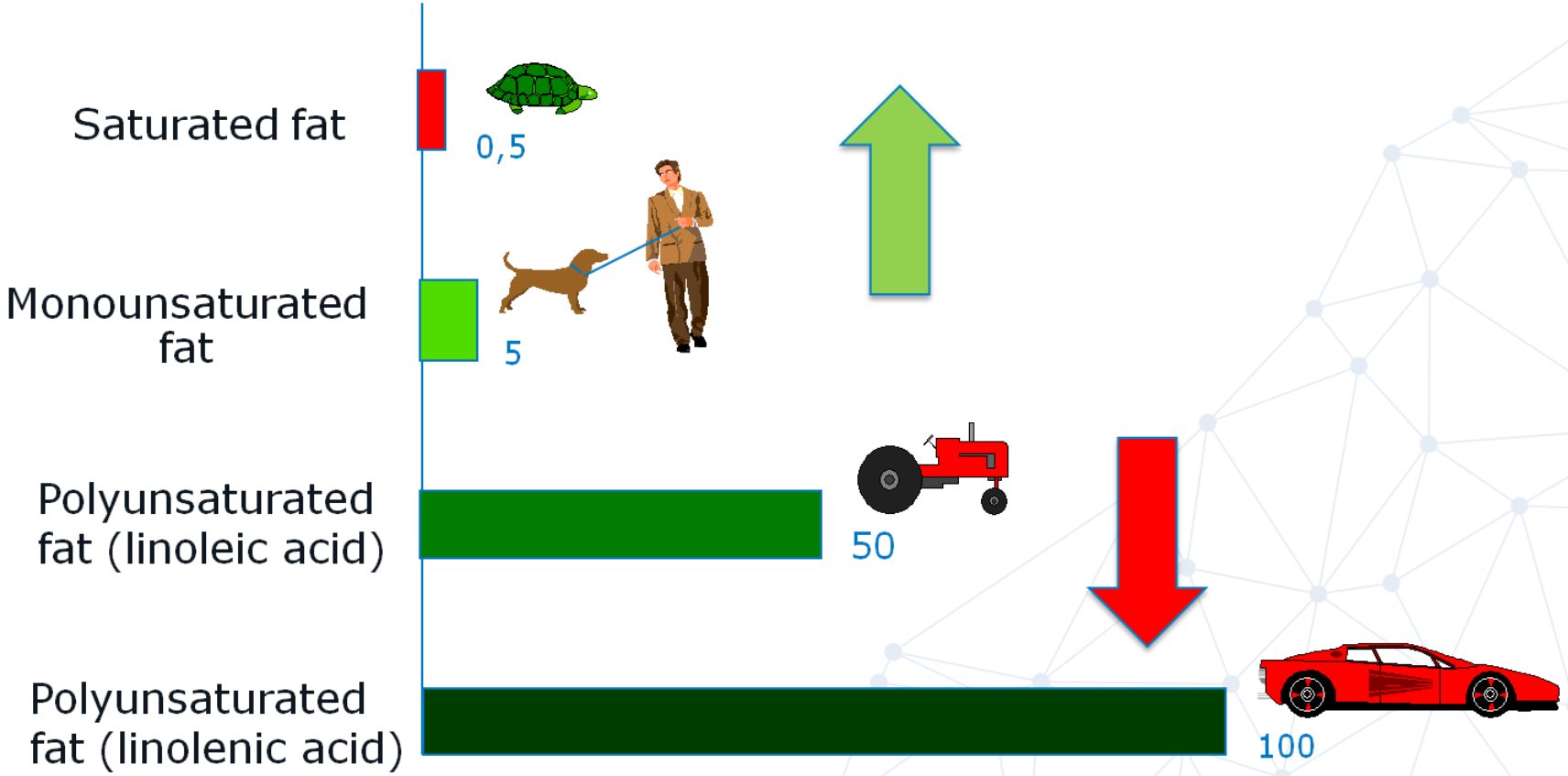
- During storage: avoid water and humidity
  - Keep containers closed and store cool and dry
- In the formulation: Avoid strong bases or acids
  - Keep the pH between 4 – 8
- Avoid lipase activity
  - Typically an effect of microbial contamination
- Short-chain triglycerides (coconut/palm kernel oils) are more sensitive than long-chain triglycerides (palm/rapeseed/shea butter)



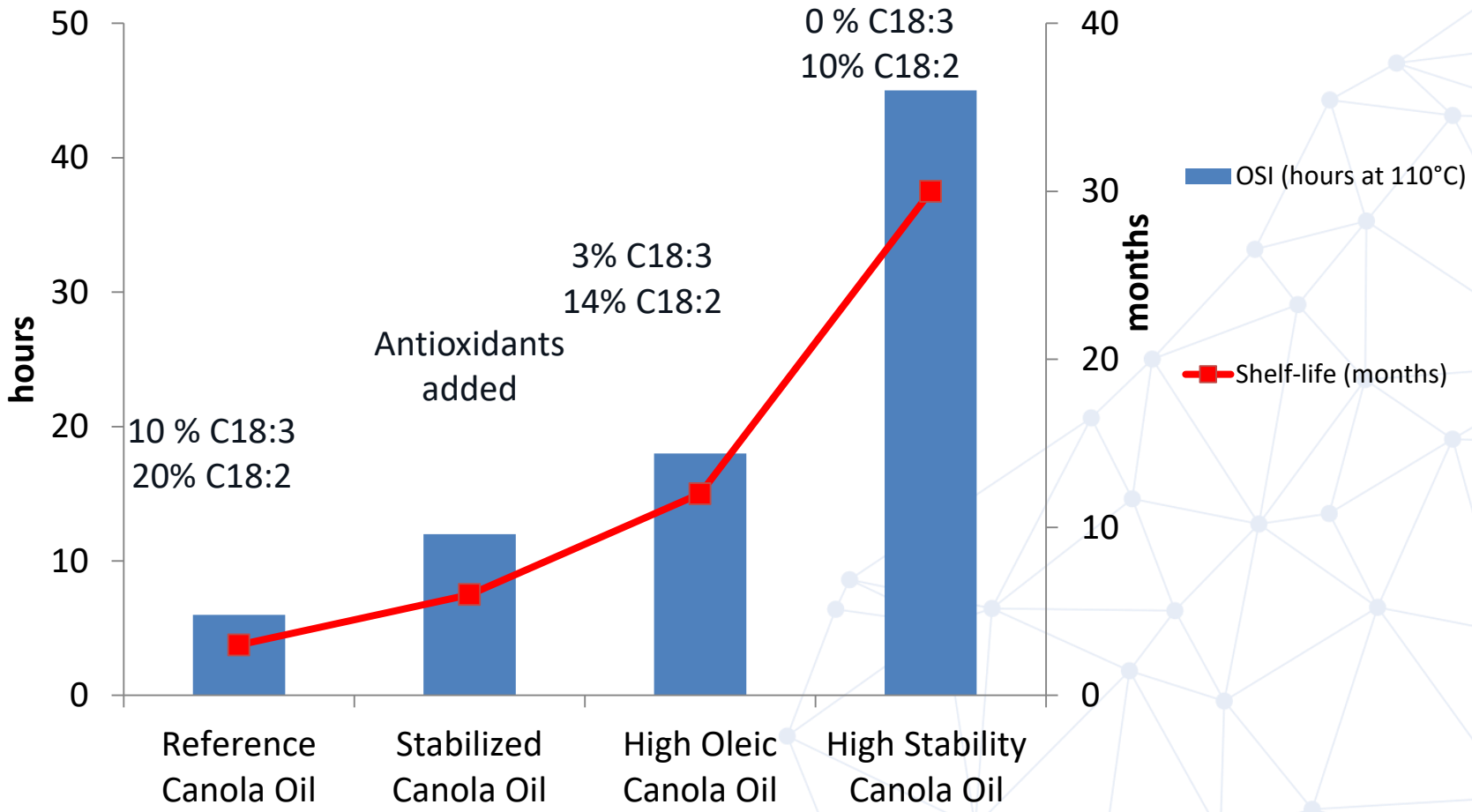
Oxidation of unsaturated lipids – Decreasing Shelf Life



Oxidation rate depends on fatty acid composition



Oxidative stability is dependent on fatty acid composition and antioxidants

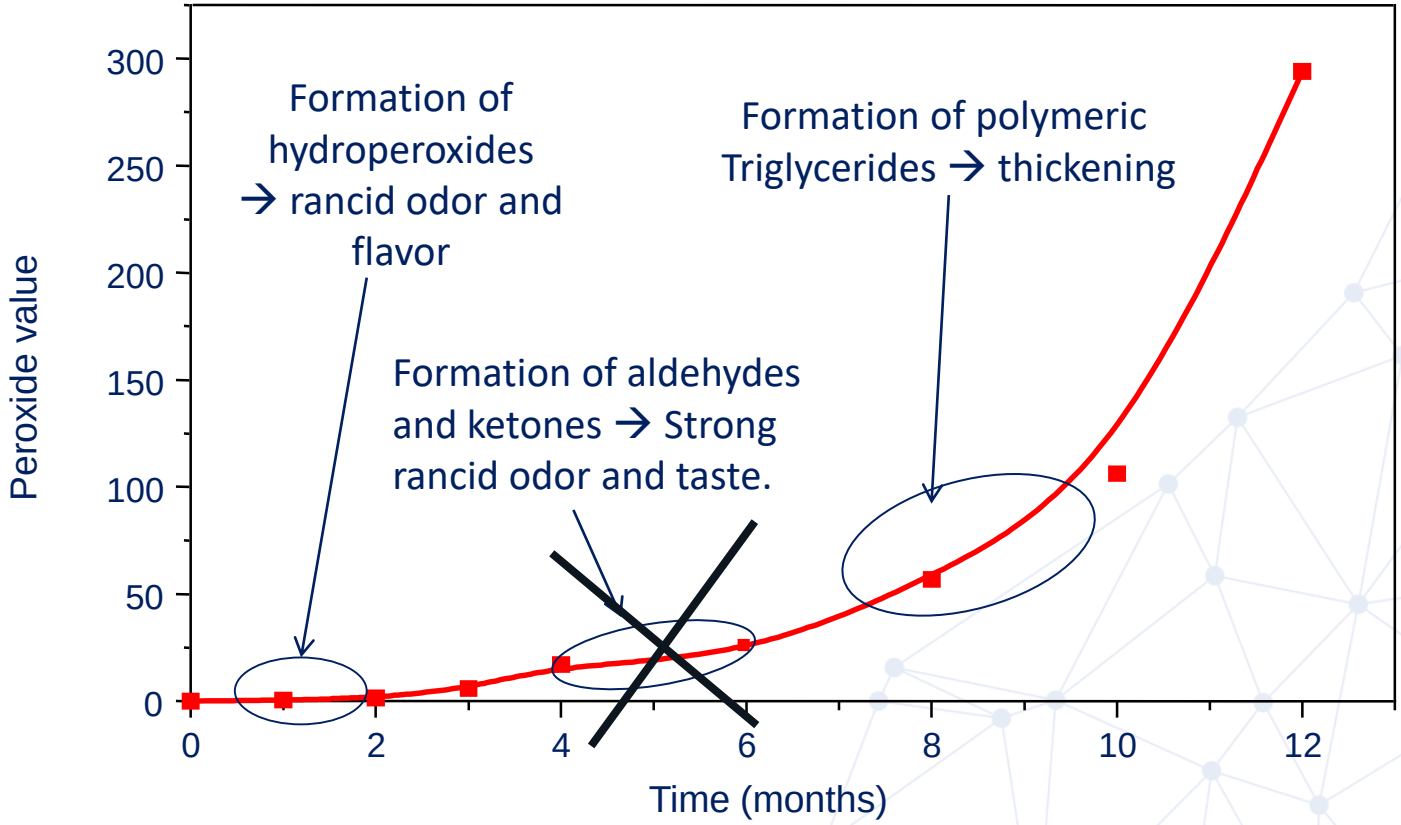


How is the shelf-life affected by oxidation?

- Oxidation products can be smelly
  - Volatile, unsaturated aldehydes and hydrocarbons
  - Odor profile depends on oxidation pathway and starting composition (origin of raw material)
- Oxidation products are pro-oxidative
  - Autocatalysis, increases oxidation rate
- Oxidation depletes the content of Omega-3/Omega-6 fatty acids and tocopherols
  - Loss of skin functionality
- Oxidation products can be irritant and/or inflammatory
  - Free radicals and reactive oxygen species may cause inflammatory reactions and accelerate premature skin aging
  - Comedogenesis has been linked to oxidation products

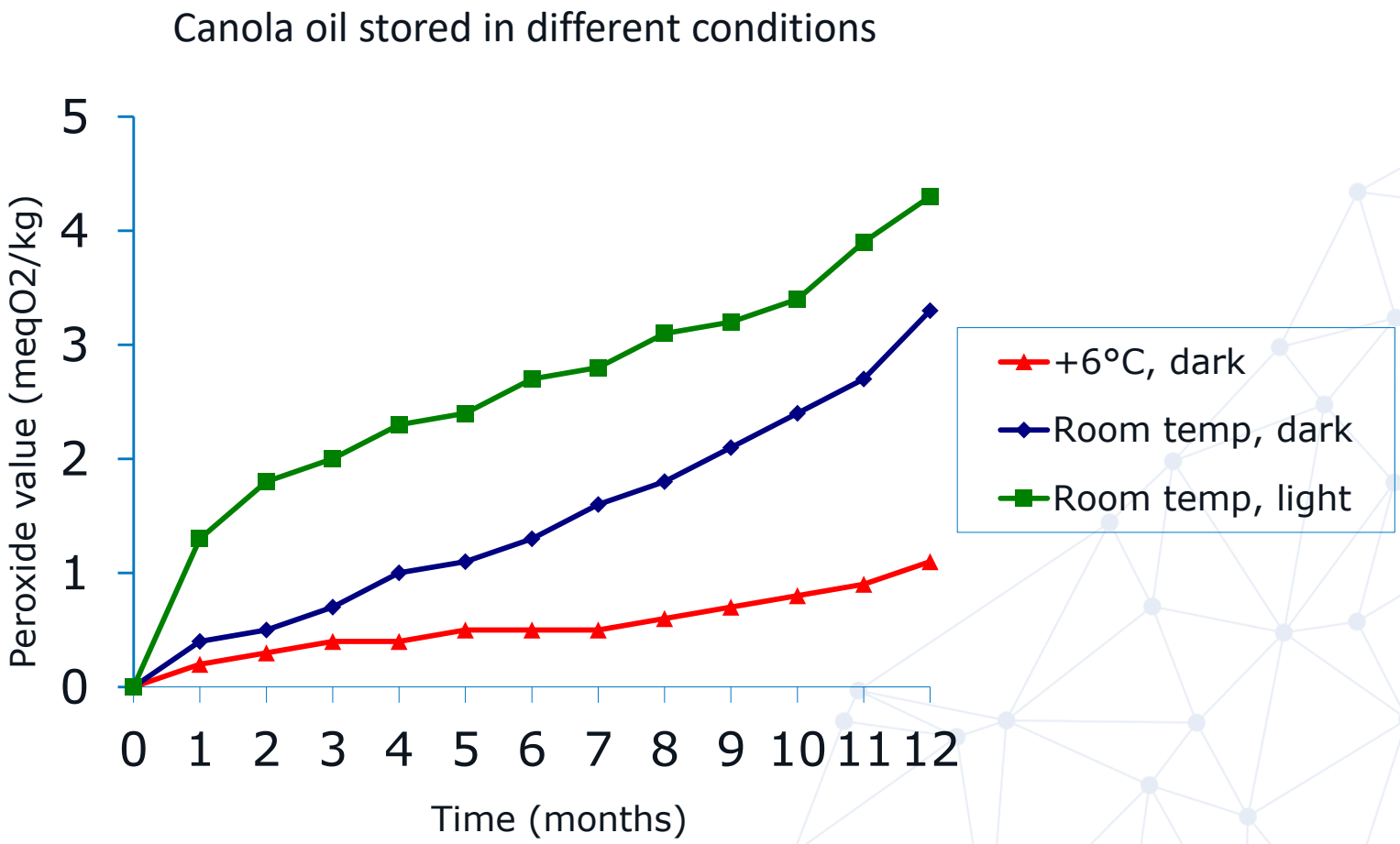
What happens during storage? Oxidative breakdown process

Sunflower seed oil stored at 22°C ; OSI (120°C) is 3 hours



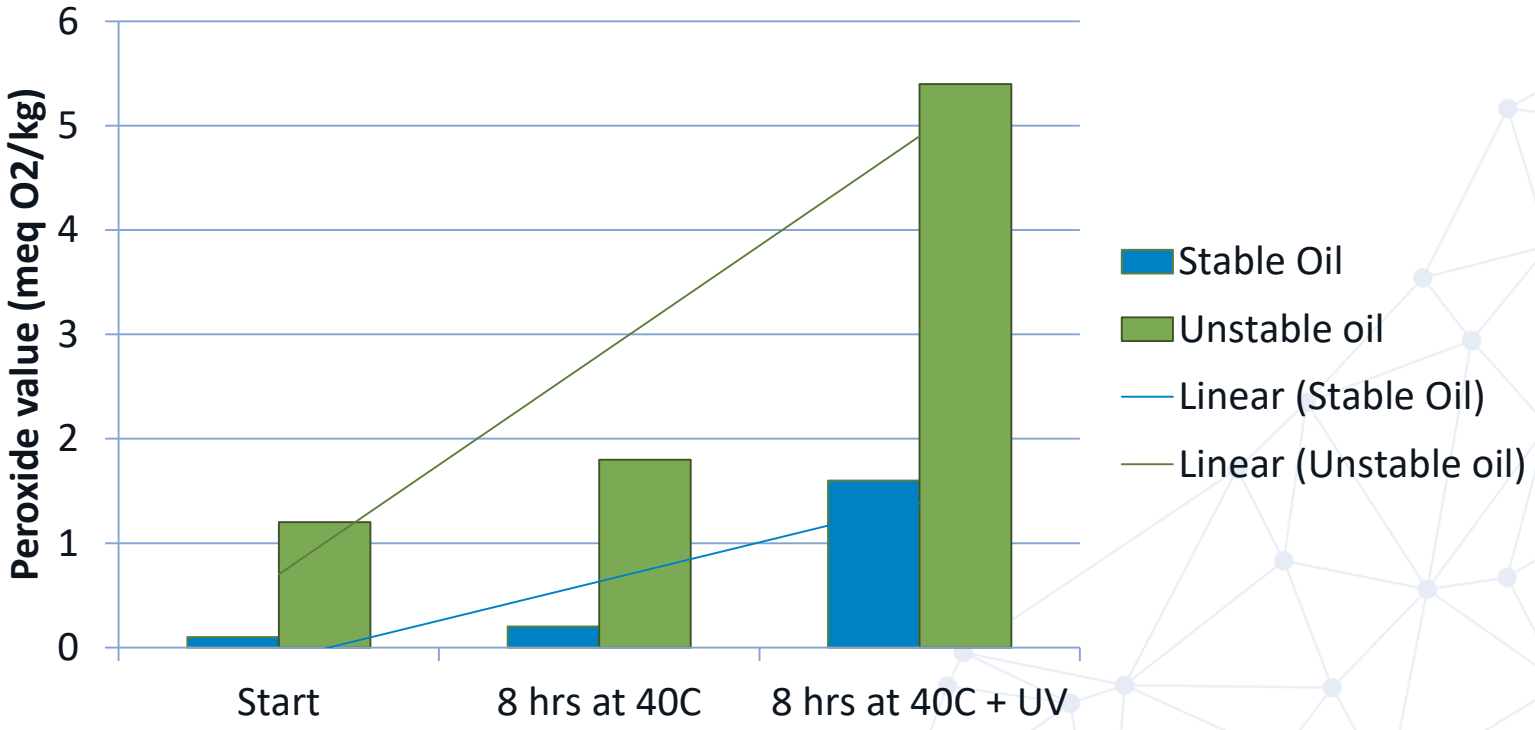
Fatty Acids (%)	C16:0	C18:0	C18:1	C18:2
Sunflower Oil	6	4	25	**63**

Why store cool and dark?



Oxygen and UV-radiation triggers autoxidation of oils and is faster at higher temperature

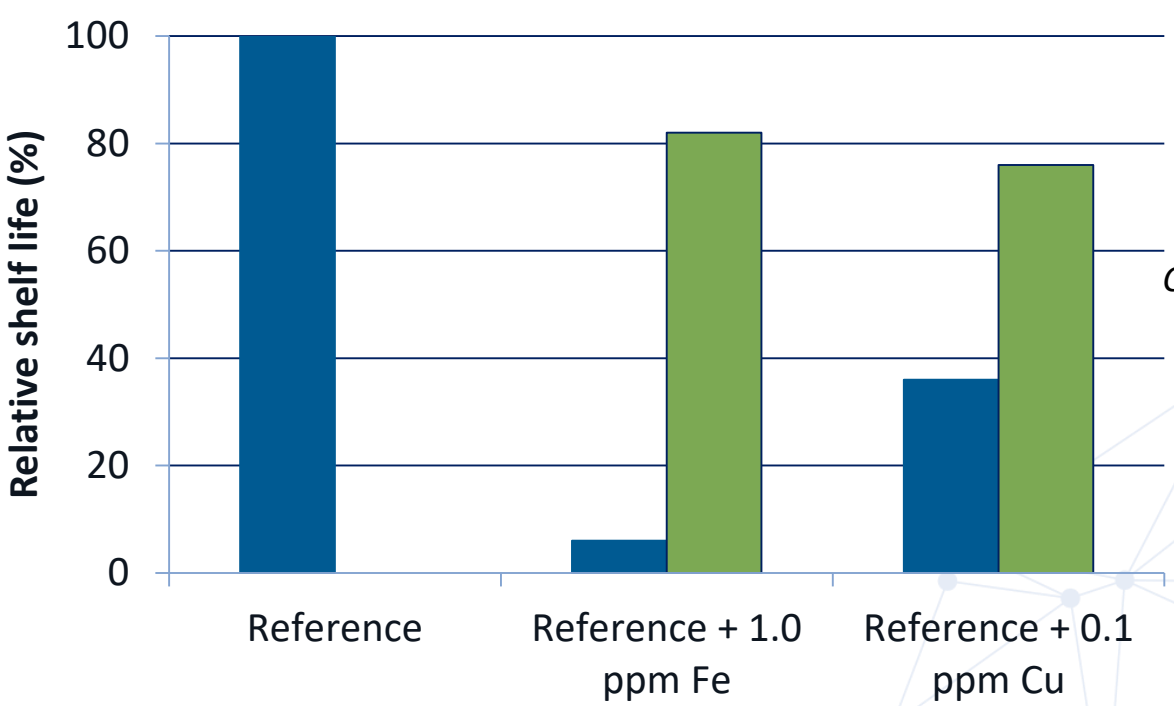
Influence of temperature and light



Important for many products like day creams / lotions, sun & after sun care products, for all ages and skin types!

Influence of metal ions

- → Metal ions induce oxidation and reduce shelf life

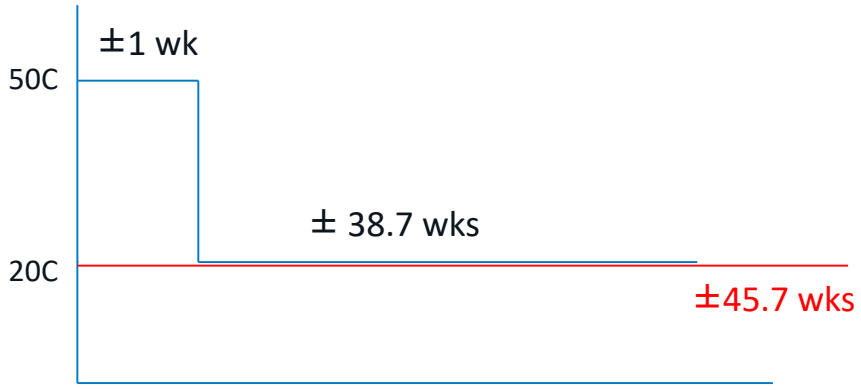


Canola oil + 200 ppm alpha-tocopherol

AAK Ingredients : <0.5 ppm Fe and <0.05 ppm Cu

Can I leave a vegetable oil for 1 week in a heating room at 50°C and what will happen to the shelf-life?

Liquid Shea		
(TC)	hours	weeks
110	**15**	
100	30	
90	60	
80	120	
70	240	
60	480	
50	**960**	
40	1920	
30	3840	
20	**7680**	**45.7**



1 week at 50C is 168 hrs at 50C ; 168/960 *100 = 17.5 %

leaves 82.5 % at 20C ; 82.5/100 * 7680 hrs = 6336 hrs

→ Changed total shelf-life to 6504 hrs = 38.7 weeks

Lost 15.4% of shelf-life

NB all values are estimated on original OSI value at 110C and have to be regarded as broad indications only

But what about an oil with lower stability? Can I leave a Sunflower Oil for 1 week in a heating room at 50°C? What will happen to the shelf-life?

1 week at 50C is 168 hrs at 50C
168/384 *100 = 43.8 %

leaves 56.2% at 20C
56.2/100 * 3072 hrs = 1728 hrs

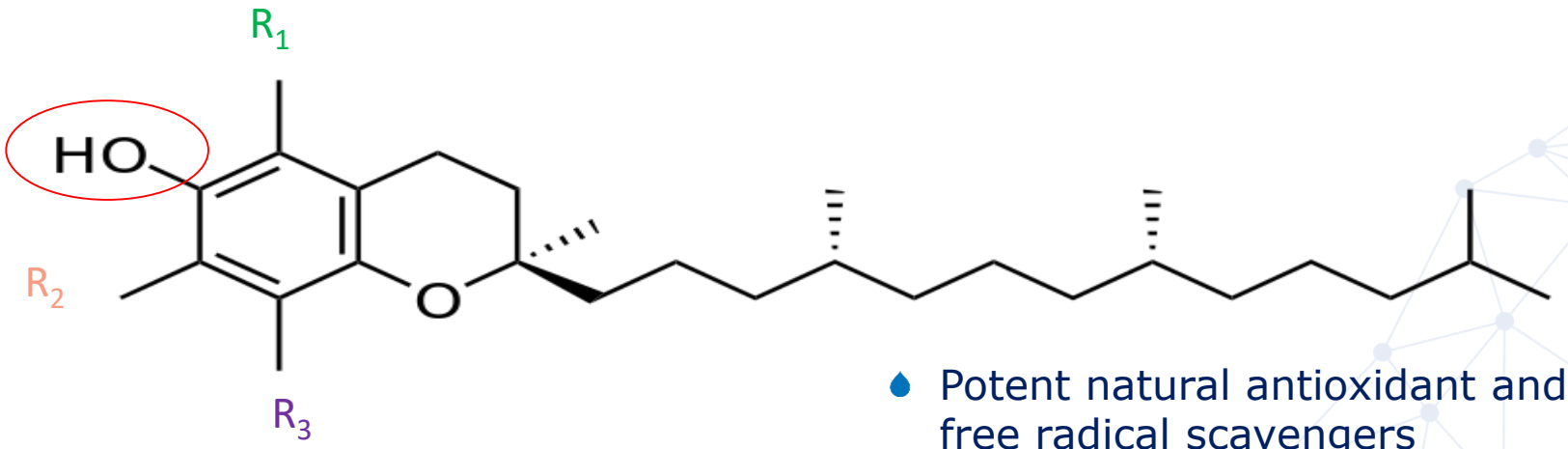
Changed total shelf-life to 1896 hrs = 11.3 weeks

Lost 38.2% of shelf-life

Sunflower oil		
(TC)	hours	weeks
120	3	
110	**6**	
100	12	
90	24	
80	48	
70	96	
60	192	
50	**384**	
40	768	
30	1536	
20	**3072**	**18.3**

NB all values are estimated on original OSI value at 110C and have to be regarded as broad indications only

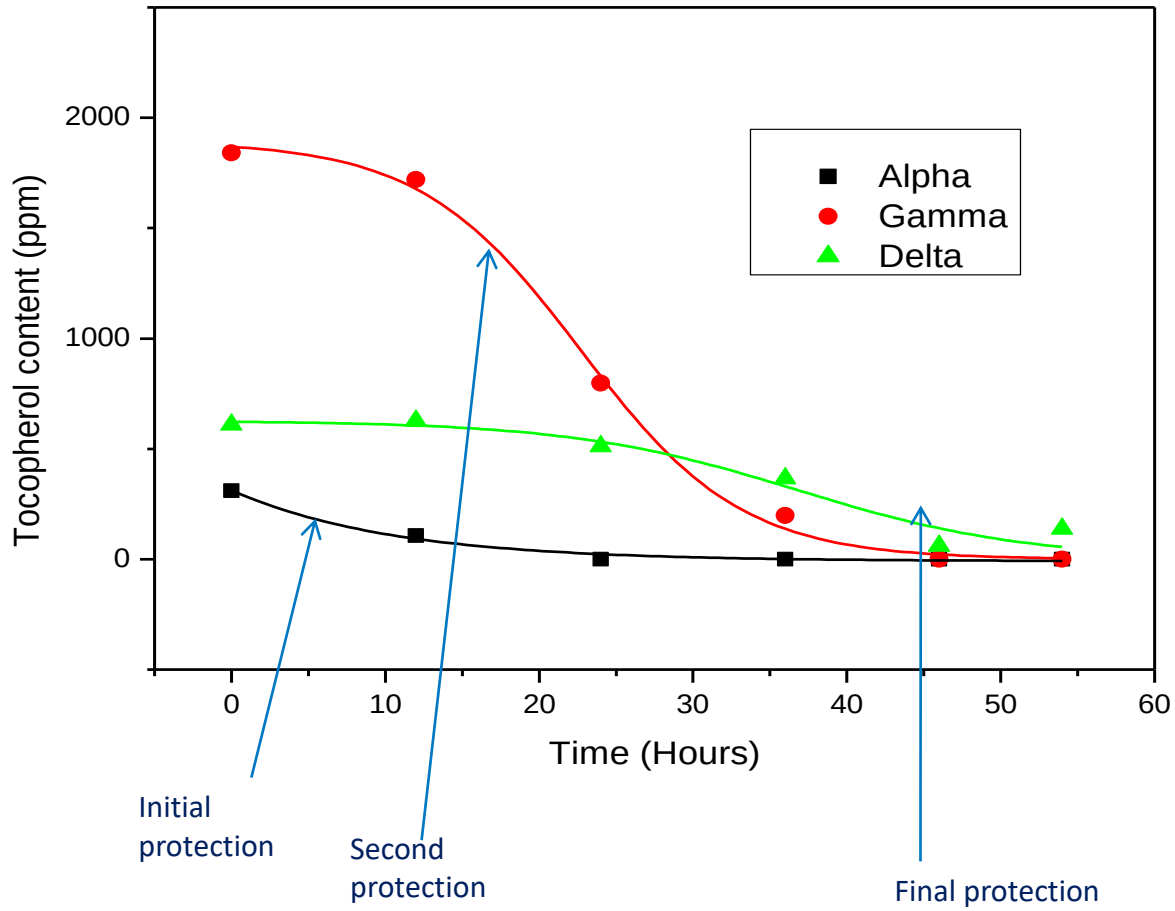
Tocopherols – Vitamin E



Form	R1	R2	R3
Alpha	Me	Me	Me
Beta	Me	H	Me
Gamma	H	Me	Me
Delta	H	H	Me

- Potent natural antioxidant and free radical scavengers
- Natural vitamin E (d-alpha tocopherol) is a mix of 8 different molecules
- Synthetic (dl-alpha tocopherol) is "pure" alpha tocopherol
- Tocopherol acetate needs hydrolysis for activation

Mix of natural tocopherol isomers gives prolonged protection



Fractionated soybean oil analysed during an OSI experiment at 120°C

Which tocopherols are present in vegetable oils?

Tocopherol content is determined by plant origin and oil processing

	Alpha (mg/kg)	Gamma (mg/kg)	Delta (mg/kg)
Soybean oil	10-350	400-2400	150-950
Rapeseed / Canola oil	100-300	300-750	10-20
Maize oil	25-575	270-2470	25-75
Palm oil **Tocotrienols**	5-185 120-150	5-35 260-300	≤70 ≤70
Sunflower oil	350-700	10-50	1-10

Steam distillation

Achieving stability and long shelf life

- Food grade oils are intended for consumption and not to be put on the skin and exposed to outdoor conditions
- Besides oxidation by-products, food grade refined oils may also contain other impurities that cause odour and colour, tolerable in food but not in cosmetics.
- Non-refined, cold pressed oils, may contain high content of breakdown products, peroxides and free radicals, proteins, pesticides, metals, coloured components and other environmental impurities influencing the shelf life and functionality.

Conclusion

- Use refined, deodorised and fresh oils and fats
  - Avoid mixing old and new batches
  - Make sure that the raw materials have low contaminant and metal content
  - Keep pH 4-8

- The fatty acid composition in the oil phase is important
  - Use high stability vegetable oils
  - Recommended: Linolenic acid content < 1% and/or Linoleic acid content < 10% in the formulation
  - Combine water-soluble, interfacial and oil soluble antioxidants

- Protect against UV, oxygen and high temperatures
  - Store dark, cold and dry before production
  - Avoid intense or prolonged heating during production
  - Use non-transparent packaging of final product