A biobased feedstock renaissance:

Improving ingredient sustainability and functionality with castor-derived precursors

Presented by **Michael J. Fevola, Ph.D.**

Keeping It Green in Personal Care
RSC Formulation Science & Technology Group
Online Symposium
2 March 2021

INOLEX

Green Chemistry is core to sustainable ingredient innovation

Our goal is to provide ingredients that deliver objective, measurable improvements in performance, consumer preference, and sustainability.

Green Chemistry encourages:

- **Safe, smart chemistry with sophisticated performance**; efficacy and efficiency
- Effective use of **renewable plant-based feedstocks**; new biobased alternatives
- Articulating and minimizing trade-offs to avoid hidden costs/consequences of "*natural*"

INOLEX

Anastas, P. T.; Warner, J. C. Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998.

Our philosophy is deeply rooted in Green Chemistry and Life Cycle Thinking

1. Feedstock Sourcing

Biobased and renewable feedstocks with a traceable and sustainable supply chain.

2. Ingredient Manufacture

Efficient use of energy and water with minimal emissions and waste generation.

3. Ingredient Shipping

Reduced shipping impacts from a global supply network and high active level ingredients.

4. Product Manufacture

Improved manufacturing efficiency from non-hazardous and easy to process ingredients.

5. Consumer Use

Safe, gentle, and non-toxic ingredients that support compelling claims with perceivable benefits.

6. End of Life

Ingredients that are biodegradable, nonpersistent, and non-toxic to aquatic life.

Feedstock diversification reduces impacts and mitigates risks

Purposeful Diversification

- Reduces eco-impact
- Improves social welfare
- Enhances product performance

2012

- INOLEX joins the **Roundtable on Sustainable Palm Oil**

2016

- INOLEX launches non-palm feedstock product line, **SustOleo**™, with a range of feedstock sources

2019

- INOLEX continues to use diverse feedstock plants in new product launches, including coconut-derived **SustOleo**™ **TL** and brassica-derived **AminoSensyl**™ **HC**

2020

- INOLEX converts to **100% RSPO Mass Balance** certified palm-derived products

Overview of today's topics

- *Ricinus communus* (castor) seed oil as a sustainable source of molecular precursors
- Methylheptylglycerin (MHG) – the first biobased branched C_8 glyceryl ether
- Capryloyl Glycerin/Sebacic Acid Copolymer – 100% biobased and readily biodegradable polyester with unique versatility

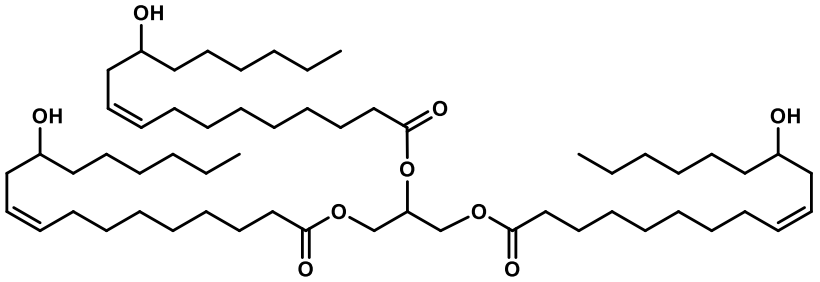
Castor as an oil seed crop

- India is leading global producer (>90%)
- Does not compete with food crops/oils
- Thrives in wide variety of environments
- Moderate land yields
  - Rainfed: 350 – 650 kg oil/ha/yr
  - Irrigated: 800 – 1200 kg oil/ha/yr
- Industry focus on improving sustainability
  - 2016: ‘Project Pragati’ Sustainable Castor Initiative
  - 2019: Sustainable Castor Association
  - 2020: Sustainable Castor Caring for Environmental and Social Standards (SuCCESS) Code

https://www.altenergymag.com/article/2011/01/a-bean-called-castor-can-cut-carbon-fuel-the-future/825, accessed 26 Feb 2021.
https://castorsuccess.org/, accessed 26 Feb 2021.

Castor oil is essential to cosmetics and personal care

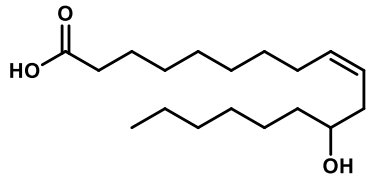
- Over 300 different ingredients (INCI Names) directly derived from castor oil or its C_{18} fatty acids
- Functions include emollients, emulsifiers, film formers, and surfactants



***Ricinus communs* (Castor) Seed Oil and Derivatives**

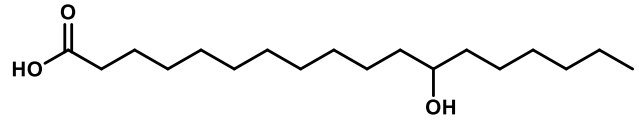
132 INCI Monographs

- Hydrogenates
- Simple/Complex Esters
- Ethoxylates
- (Co)polymers



Ricinoleic Acid and Derivatives

93 INCI Monographs



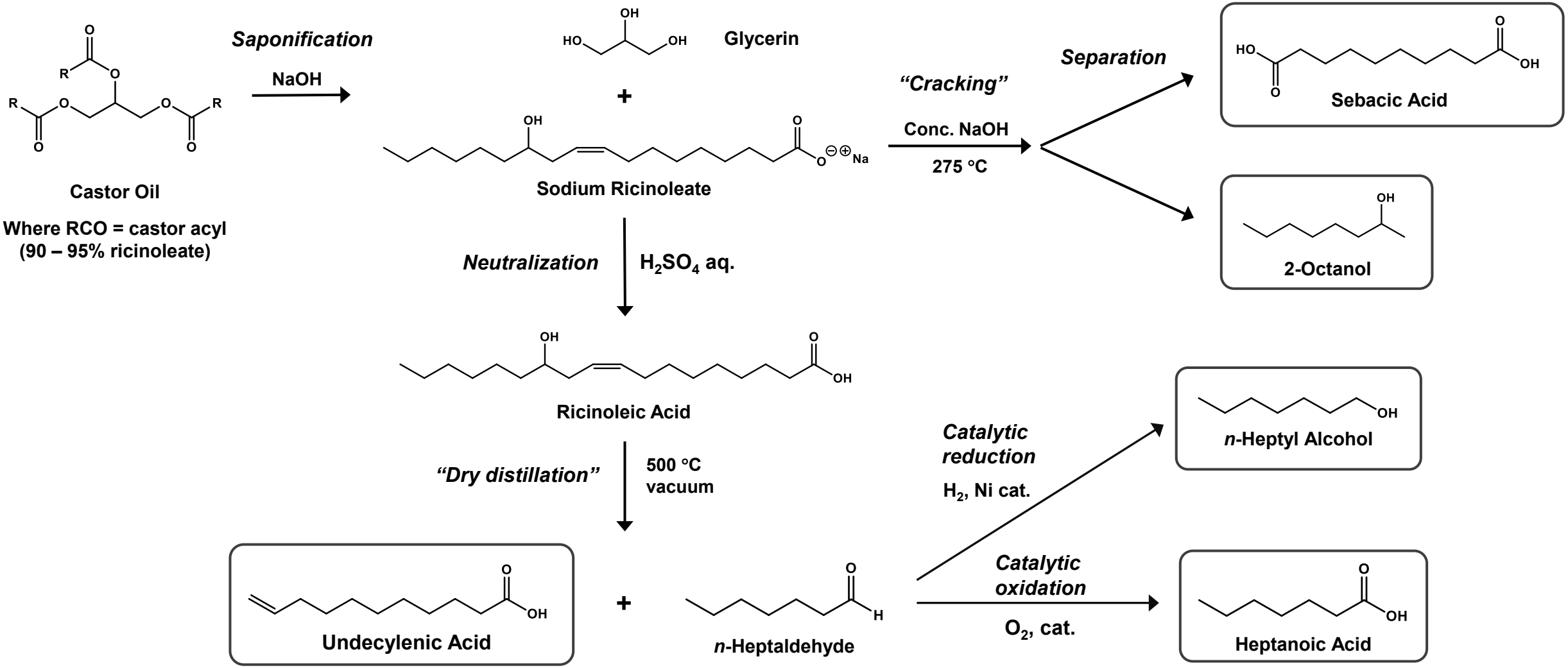
Hydroxystearic Acid and Derivatives

87 INCI Monographs

- Salts
- Amides
- Simple/Complex Esters
- Ethoxylates
- (Co)polymers

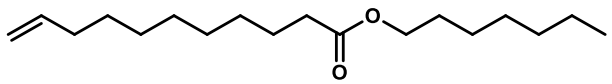
Personal Care Products Council On-Line INFOBASE, https://online.personalcarecouncil.org/jsp/Home.jsp, accessed 25 Feb 2021.

Sustainable castor oil yields many useful starting materials



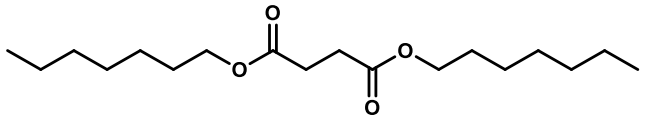
Kudchadker, A. P.; Kudchadker, S. A.; Singh, D. K. Castor Oil Cracking Products, In *Encycl. Chem. Process Design*, Vol. 6, Marcel Dekker, Inc.: New York, 1978, pp 401 – 419.

100% biobased, high-performance ingredients from castor



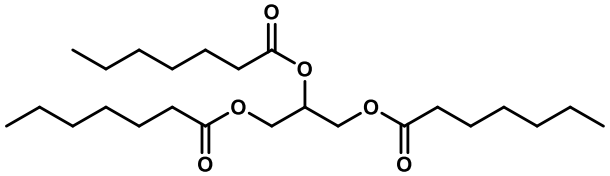
LexFeel™ Natural

Heptyl Undecylenate



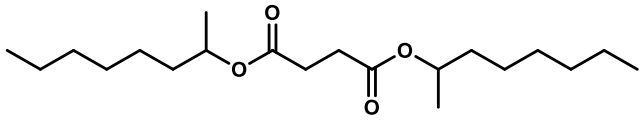
LexFeel™ N Series MB

Diheptyl Succinate (and) Capryloyl Glycerin/ Sebacic Acid Copolymer



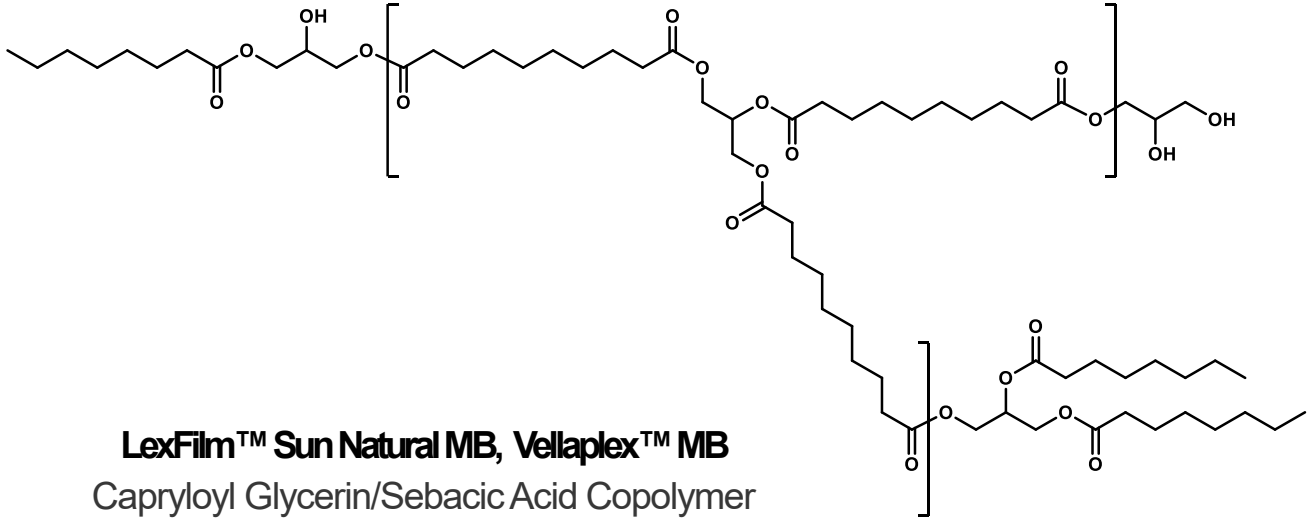
SustOleo™ MCT

Triheptanoin



SustOleo™ DCS

Diisooctyl Succinate

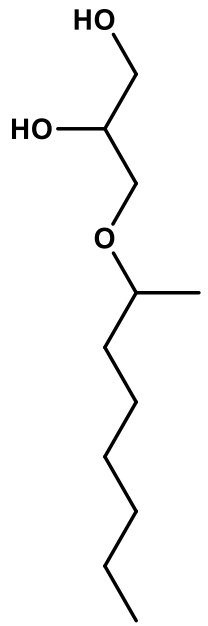


LexFilm™ Sun Natural MB, Vellaplex™ MB

Capryloyl Glycerin/Sebacic Acid Copolymer

Sustainable alternatives to silicones and petro-based ingredients for SKIN, SUN, and HAIR CARE

Lexgard® Natural MHG MB: Methylheptylglycerin



3-[(1-Methylheptyl)oxy]-1,2-propanediol

CAS No. 182015-50-5

INCI: Methylheptylglycerin

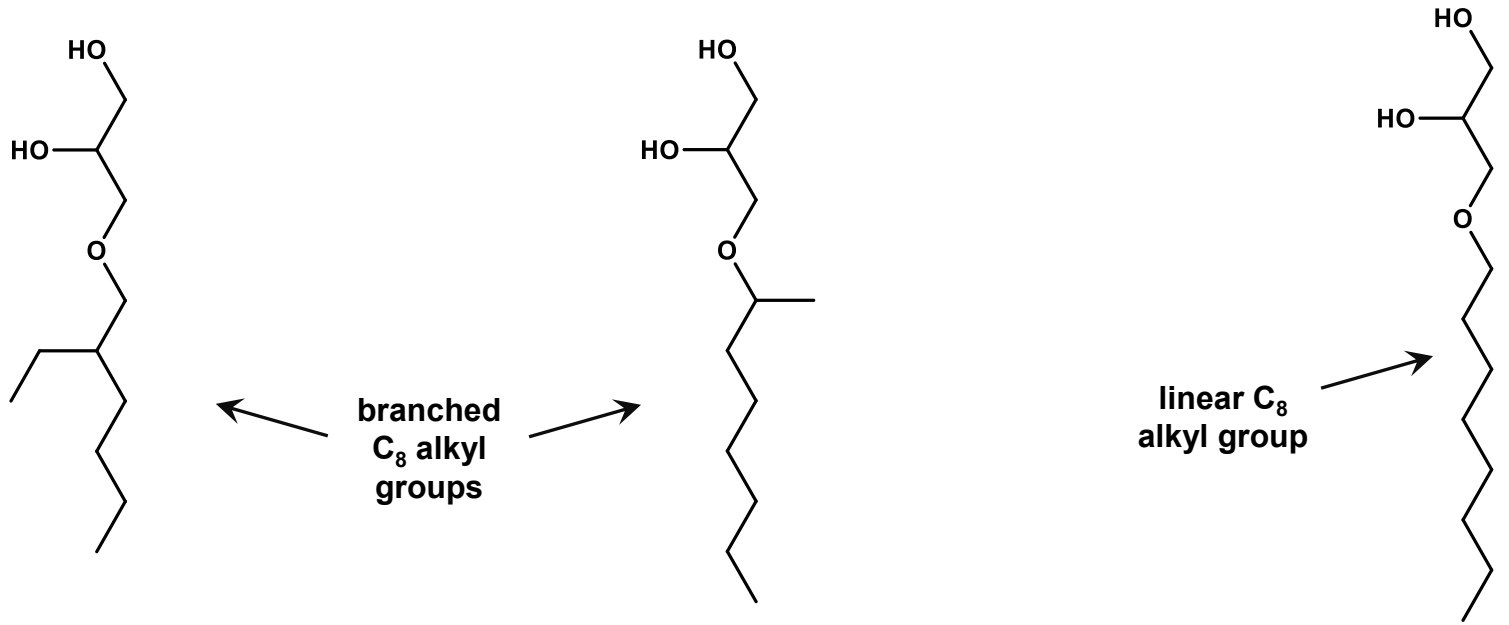
- MHG is the first biobased branched C_8 glyceryl ether
- Medium-chain terminal diol (MCTD) → *multifunctional*
- Nonionic, amphiphilic compound – surface/interfacial activity aids in wetting, solubilization
- Hurdle functions contribute preservation benefits:
  - Enhances cell permeability for biostatic effect (not biocidal)
  - Reduces water activity

Methylheptylglycerin: A natural analog of Ethylhexylglycerin

C_8 alkyl glyceryl ethers

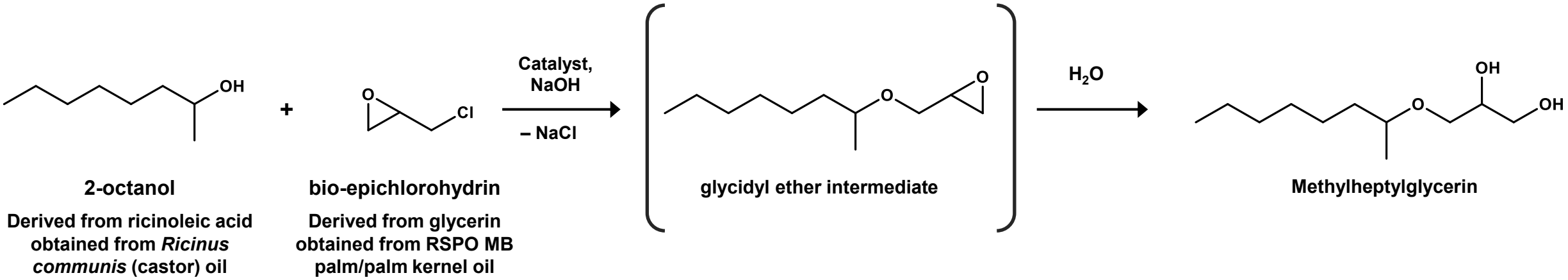
Formula: $C_{11}H_{24}O_3$

MW: 204.31 g/mol



INCI Name	Ethylhexylglycerin	Methylheptylglycerin	Caprylyl Glyceryl Ether
C_8 source	Petrochemical	Castor	Palm Kernel/Coconut
Biobased content	0%	100%	100% (if bio-ECH used)
Form at 20 °C / Melt Temp	Liquid / –13 °C	Liquid / –15 °C	Solid / 24 °C
Log K_{OW} (calc.)	1.93	1.85	1.95
Reported Functions	Deodorant, Skin Conditioning	Deodorant, Humectant, Skin Conditioning	Surfactant – Cleansing, Foam Boosting

Methylheptylglycerin (MHG) synthesis



2-octanol

Derived from ricinoleic acid obtained from *Ricinus communis* (castor) oil

bio-epichlorohydrin

Derived from glycerin obtained from RSPO MB palm/palm kernel oil

glycidyl ether intermediate

Methylheptylglycerin

- Utilizes same manufacturing route as ethylhexylglycerin
- 100% biobased (plant) carbon by ^{14}C radiocarbon dating – USDA BioPreferred® certified
- 100% naturally-derived per ISO 16128 standard, COSMOS certified
  - Allowed reactions, i.e. etherification and hydrolysis
  - Readily biodegradable (OECD 301B)

Patent pending

MHG protects well against bacteria and yeast

Preservation efficacy (PE) criteria:

USP 51 < PCPC < EP-B < EP-A

Screening Formula:
Natural O/W Lotion Base

INCI Name	Formula Wt%
Water	Q.S. to 100.00
Triheptanoin	5.00
Heptyl Undecylenate	5.00
Glyceryl Stearate SE	4.00
Hydrogenated Rapeseed Oil	3.00
Glycerin	3.00
Xanthan Gum	0.30
Methylheptylglycerin	0.50 – 1.00
Citric Acid	Q.S. to pH 5.0 ± 0.2 or pH 6.5 ± 0.2

pH 5.0, unpreserved control

	Log_{10} CFU/g				
	S. aureus	*E. coli*	*P. aeruginosa*	*C. albicans*	*A. brasiliensis*
Inoculum level	6.04	6.04	6.03	5.02	5.00
Day 2	5.00	5.00	5.00	5.00	3.41
Day 7	4.11	5.00	<1.00	5.00	3.34
Day 14	1.78	5.00	<1.00	5.00	2.61
Day 21	<1.00	5.00	<1.00	5.00	2.60
Day 28	<1.00	5.00	<1.00	5.00	2.32

FAIL FOR ALL CRITERIA

pH 5.0, 0.50% MHG

	Log_{10} CFU/g				
	S. aureus	*E. coli*	*P. aeruginosa*	*C. albicans*	*A. brasiliensis*
Inoculum level	6.04	6.04	6.03	5.02	5.00
Day 2	<1.00	<1.00	<1.00	<1.00	3.53
Day 7	<1.00	<1.00	<1.00	<1.00	3.32
Day 14	<1.00	<1.00	<1.00	<1.00	3.28
Day 21	<1.00	<1.00	<1.00	<1.00	3.28
Day 28	<1.00	<1.00	<1.00	<1.00	3.23

PASS FOR USP 51, PCPC, EP-B

pH 6.5, unpreserved control

	Log_{10} CFU/g				
	S. aureus	*E. coli*	*P. aeruginosa*	*C. albicans*	*A. brasiliensis*
Inoculum level	6.02	6.04	6.02	5.02	5.00
Day 2	5.00	5.00	5.00	5.00	3.20
Day 7	4.26	5.00	5.00	5.00	3.11
Day 14	2.62	5.00	5.00	5.00	1.90
Day 21	<1.00	5.00	5.00	5.00	<1.00
Day 28	<1.00	5.00	5.00	5.00	<1.00

FAIL FOR ALL CRITERIA

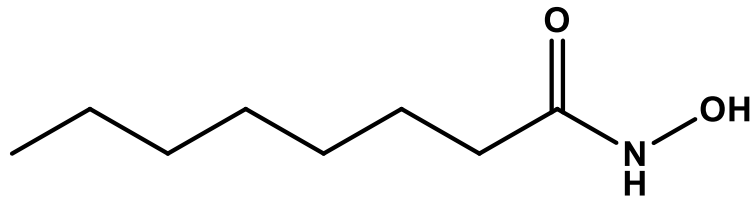
pH 6.5, 1.00% MHG

	Log_{10} CFU/g				
	S. aureus	*E. coli*	*P. aeruginosa*	*C. albicans*	*A. brasiliensis*
Inoculum level	6.18	6.04	6.02	5.02	5.00
Day 2	3.15	<1.00	<1.00	<1.00	2.97
Day 7	<1.00	<1.00	<1.00	<1.00	2.91
Day 14	<1.00	<1.00	<1.00	<1.00	2.59
Day 21	<1.00	<1.00	<1.00	<1.00	2.38
Day 28	<1.00	<1.00	<1.00	<1.00	1.95

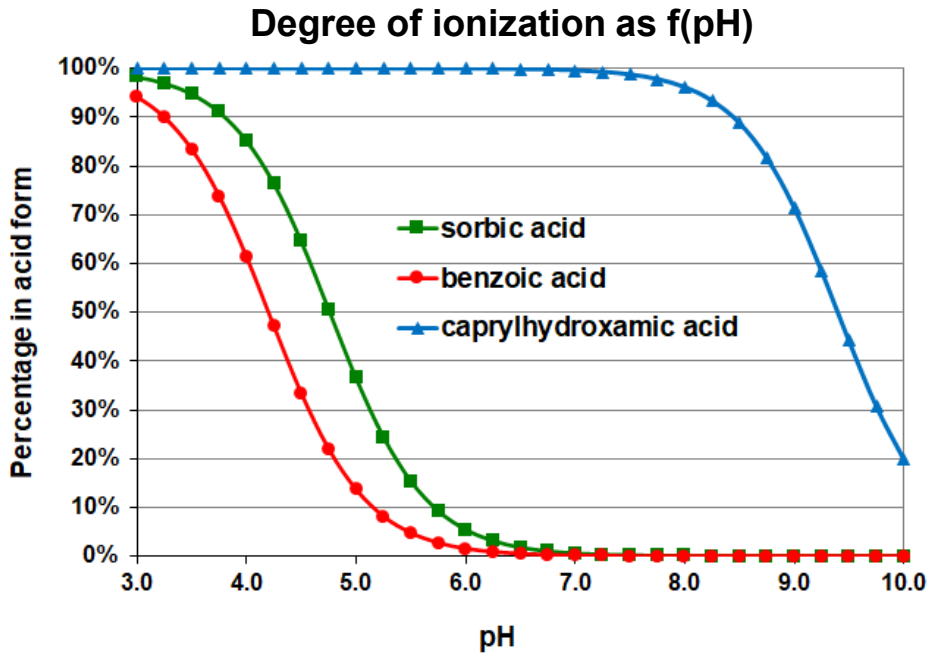
PASS FOR USP 51, PCPC, EP-A

Boosting with Caprylhydroxamic Acid (CHA)

- CHA is a 100% naturally-derived chelating agent based on C_8 fatty acid (coconut)
- CHA provides three hurdles from one ingredient:
  - **Chelating agent:** sequesters essential nutrients for microorganisms
  - **Organic acid:** CHA $pK_a \approx 9.4$, thus it retains efficacy above neutral pH
  - **Medium chain amphiphile:** similar character to MCTDs (Log K_{OW} = 1.7)
- CHA combinations with MCTDs provide broad spectrum preservation efficacy, esp. against yeast and mold
  - Typical use level = 0.10 – 0.15 wt% CHA in formulation
  - Stable from pH 4 – 8 under accelerated conditions (12 wk at 40 °C)



***N*-hydroxyoctanamide**
INCI: Caprylhydroxamic Acid



US 8,993,641 B2, *Preservation of cosmetics, toiletry and pharmaceutical compositions*, assigned to INOLEX Investment Corp., 2015.

CHA boosts efficacy of MHG for stronger broad spectrum protection

Screening Formula: Natural O/W Lotion

INCI Name	Formula Wt%
Water	Q.S. to 100.00
Triheptanoin	5.00
Heptyl Undecylenate	5.00
Glyceryl Stearate SE	4.00
Hydrogenated Rapeseed Oil	3.00
Glycerin	3.00
Xanthan Gum	0.30
Methylheptylglycerin	0.70 – 1.00
Caprylhydroxamic Acid	0 – 0.15
Citric Acid	Q.S. to pH 5.0 ± 0.2 or pH 6.5 ± 0.2

pH 6.5, 1.00% MHG

	Log_{10} CFU/g				
	S. aureus	*E. coli*	*P. aeruginosa*	*C. albicans*	*A. brasiliensis*
Inoculum level	6.18	6.04	6.02	5.02	5.00
Day 2	3.15	<1.00	<1.00	<1.00	2.97
Day 7	<1.00	<1.00	<1.00	<1.00	2.91
Day 14	<1.00	<1.00	<1.00	<1.00	2.59
Day 21	<1.00	<1.00	<1.00	<1.00	2.38
Day 28	<1.00	<1.00	<1.00	<1.00	1.95

PASS FOR USP 51, PCPC, EP-A

pH 6.5, 0.70% MHG + 0.15% CHA

	Log_{10} CFU/g				
	S. aureus	*E. coli*	*P. aeruginosa*	*C. albicans*	*A. brasiliensis*
Inoculum level	6.03	6.02	6.01	5.01	5.01
Day 2	<1.00	<1.00	<1.00	<1.00	1.95
Day 7	<1.00	<1.00	<1.00	<1.00	<1.00
Day 14	<1.00	<1.00	<1.00	<1.00	<1.00
Day 21	<1.00	<1.00	<1.00	<1.00	<1.00
Day 28	<1.00	<1.00	<1.00	<1.00	<1.00

PASS FOR USP 51, PCPC, EP-A

pH 6.5, unpreserved control

	Log_{10} CFU/g				
	S. aureus	*E. coli*	*P. aeruginosa*	*C. albicans*	*A. brasiliensis*
Inoculum level	6.02	6.04	6.02	5.02	5.00
Day 2	5.00	5.00	5.00	5.00	3.20
Day 7	4.26	5.00	5.00	5.00	3.11
Day 14	2.62	5.00	5.00	5.00	1.90
Day 21	<1.00	5.00	5.00	5.00	<1.00
Day 28	<1.00	5.00	5.00	5.00	<1.00

FAIL FOR ALL CRITERIA

Addition of 0.15% CHA enhances broad spectrum efficacy and enables decreased use level of MHG

Anti-soaping effect of MHG in silicone-free emulsions

- Cationic lamellar liquid crystal emulsion (O/W)
  - Silicone: 5 wt% Dimethicone
  - Silicone-free: 5 wt% Triheptanoin (and) C13-15 Alkane
- Silicone-free exhibits severe soaping on rub-in
- 2% MHG provides same anti-soaping effect as 0.5% Dimethicone

INCI Name	Wt%	Wt%	Wt%	Wt%
Water	71.25	71.25	69.75	70.25
Triheptanoin	8.00	8.00	8.00	8.00
Dimethicone	5.00	–	0.50	–
Triheptanoin (and) C13-15 Alkane	–	5.00	5.00	5.00
Brassica Alcohol	4.00	4.00	4.00	4.00
Cetyl Alcohol	3.00	3.00	3.00	3.00
Glycerin	3.00	3.00	3.00	3.00
Brassicamidopropyl Dimethylamine	2.00	2.00	2.00	2.00
Glyceryl Stearate	2.00	2.00	2.00	2.00
Caprylyl Glycol	1.00	1.00	2.00	–
Methylheptylglycerin	–	–	–	2.00
Aspartic Acid	0.75	0.75	0.75	0.75
TOTAL	100.00	100.00	100.00	100.00

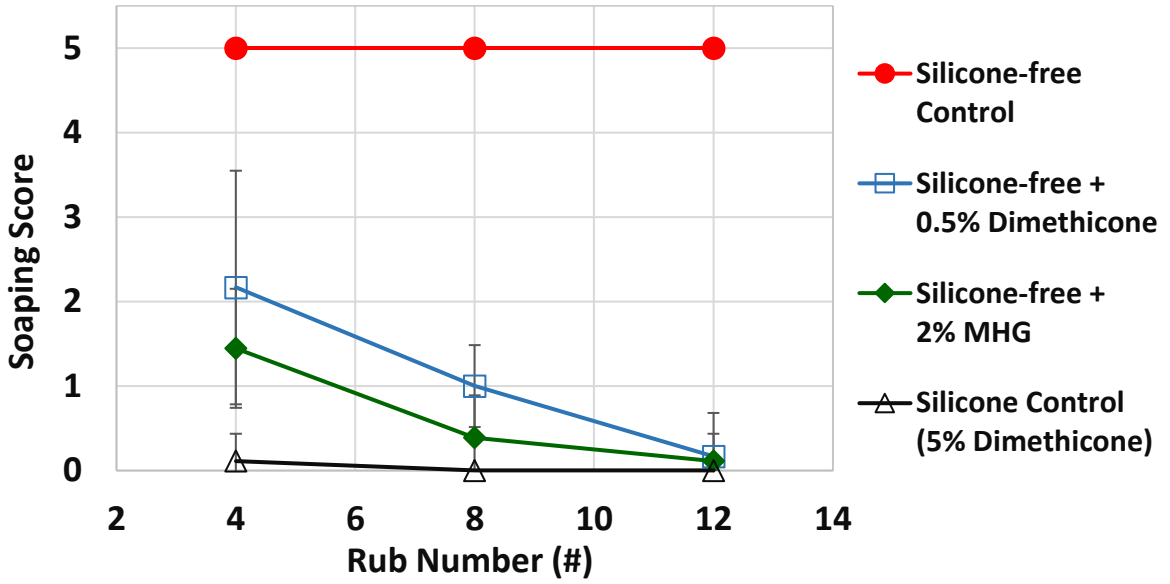


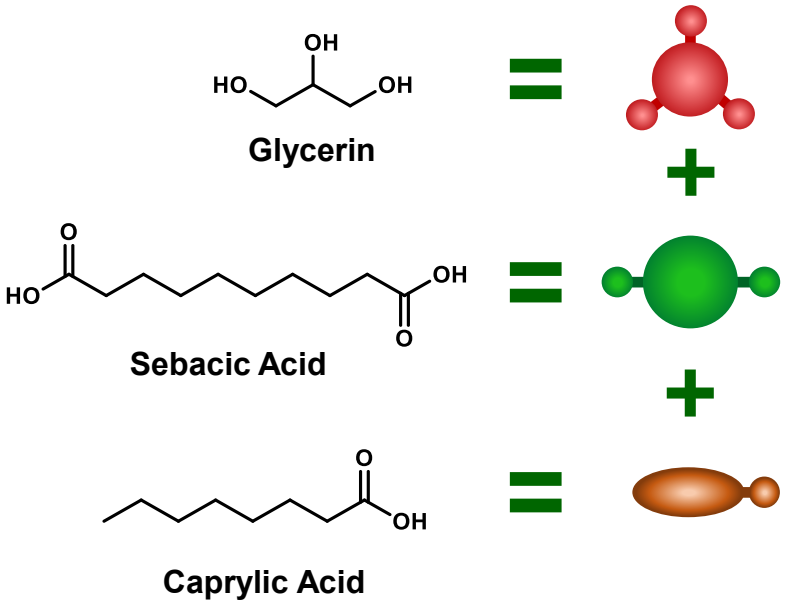
Image at Rub #8

Capryloyl Glycerin/Sebacic Acid Copolymer

100% biobased and readily biodegradable polyester with unique versatility

Capryloyl Glycerin/Sebacic Acid Copolymer (CGSAC)

Polyesters are made from an environmentally-benign condensation process – no solvents, no waste – the only byproduct is water!



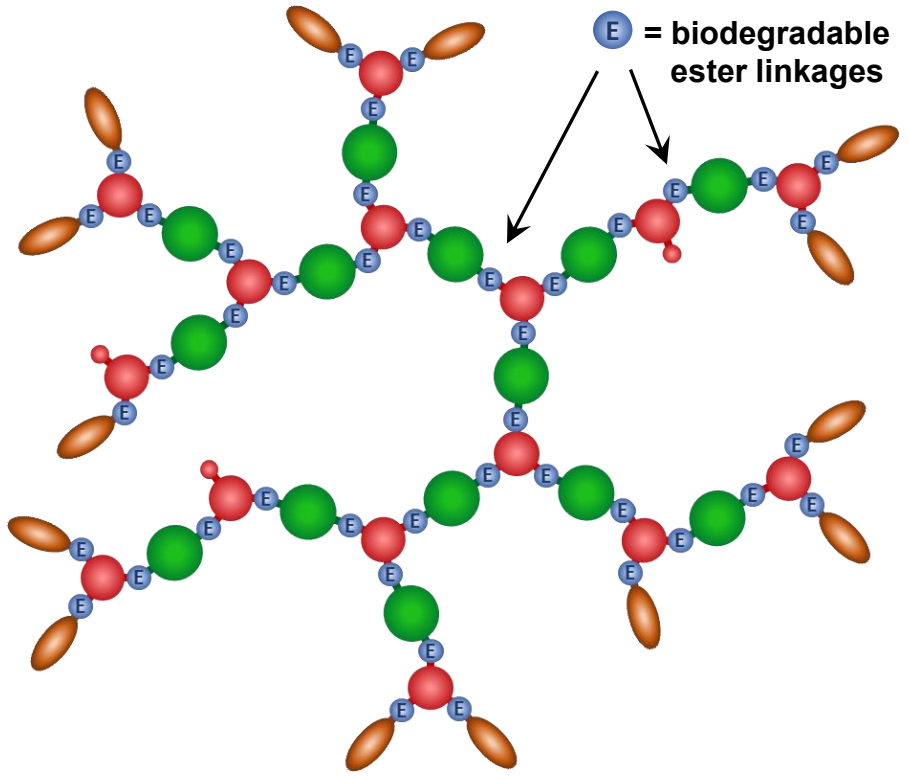
Structure controlled by:

- Feed ratios
- Process conditions
- Percent conversion

Condensation

H_2O removed

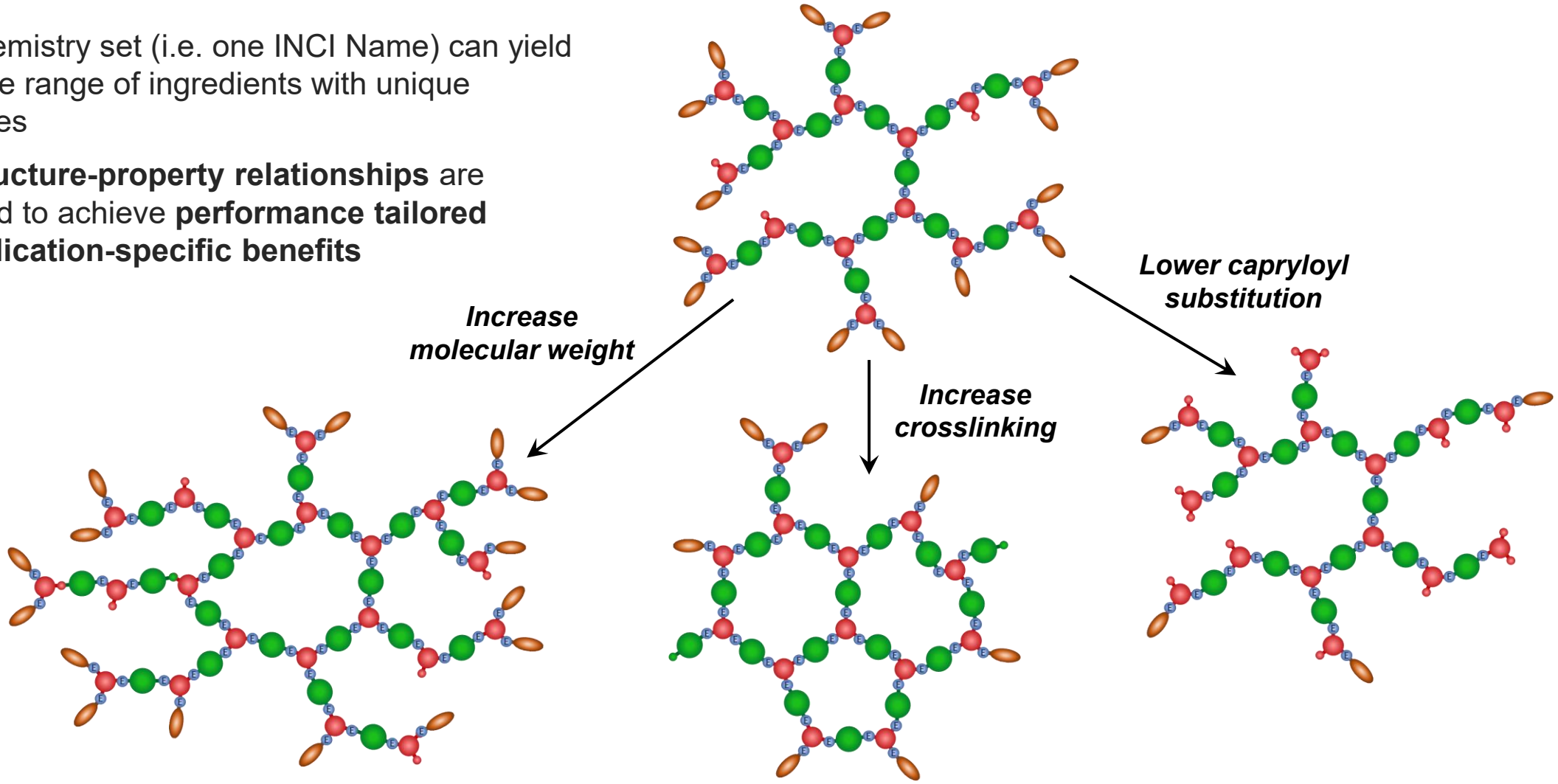
Capryloyl Glycerin/Sebacic Acid Copolymer



US 7,317,068, *Complex polyol polyester polymer compositions for use in personal care products and related methods*, assigned to Inolex Investment Corp., 2008.

Designer molecules: versatility of the CGSAC polyester platform

- One chemistry set (i.e. one INCI Name) can yield a diverse range of ingredients with unique properties
- Key **structure-property relationships** are exploited to achieve **performance tailored for application-specific benefits**

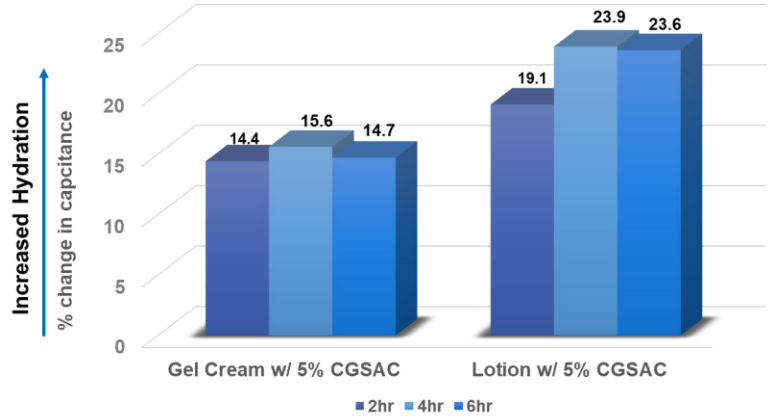


Applications of Capryloyl Glycerin/Sebacic Acid Copolymer

Capryloyl Glycerin/ Sebacic Acid Copolymer

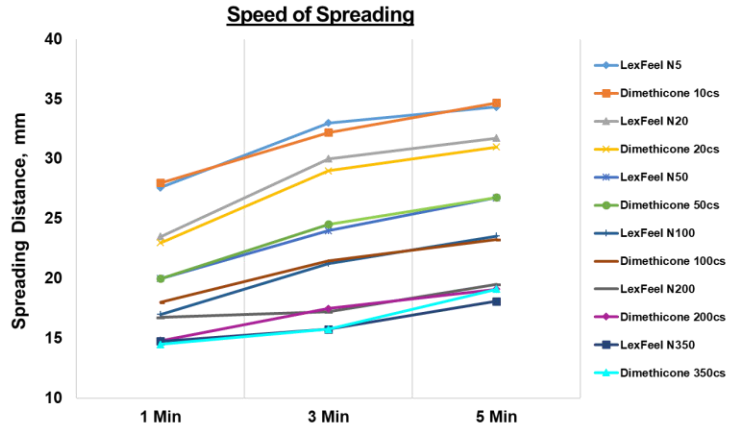
High MW, High Viscosity: Vellaplex™

Substantive film former with barrier properties



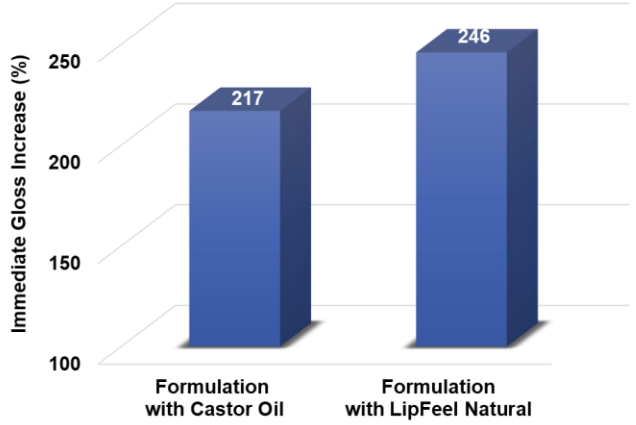
Blends with Diheptyl Succinate: LexFeel™ N Series

Alternatives for D5 and Dimethicone (5 – 350 cSt)



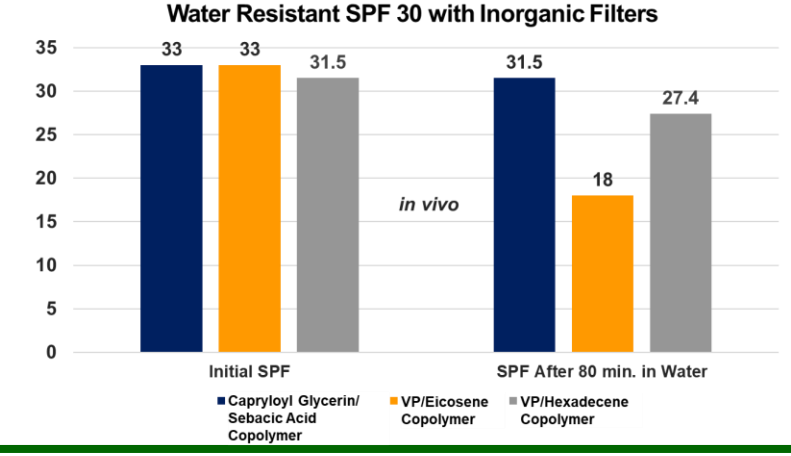
Low MW, High Hydroxyl: LipFeel Natural

Improved performance vs. castor oil for lipstick



Broad MWD: LexFilm™ Sun Natural

Film former for water-resistant sunscreens



Polyester doesn't necessarily mean *plastic*!

Aromatic Polyesters:

- Petroleum derived
- Not biodegradable
- Solids

Aliphatic Polyesters:

- Many are naturally derived
- May be solids or liquids
- Can be biodegradable and/or environmentally degradable

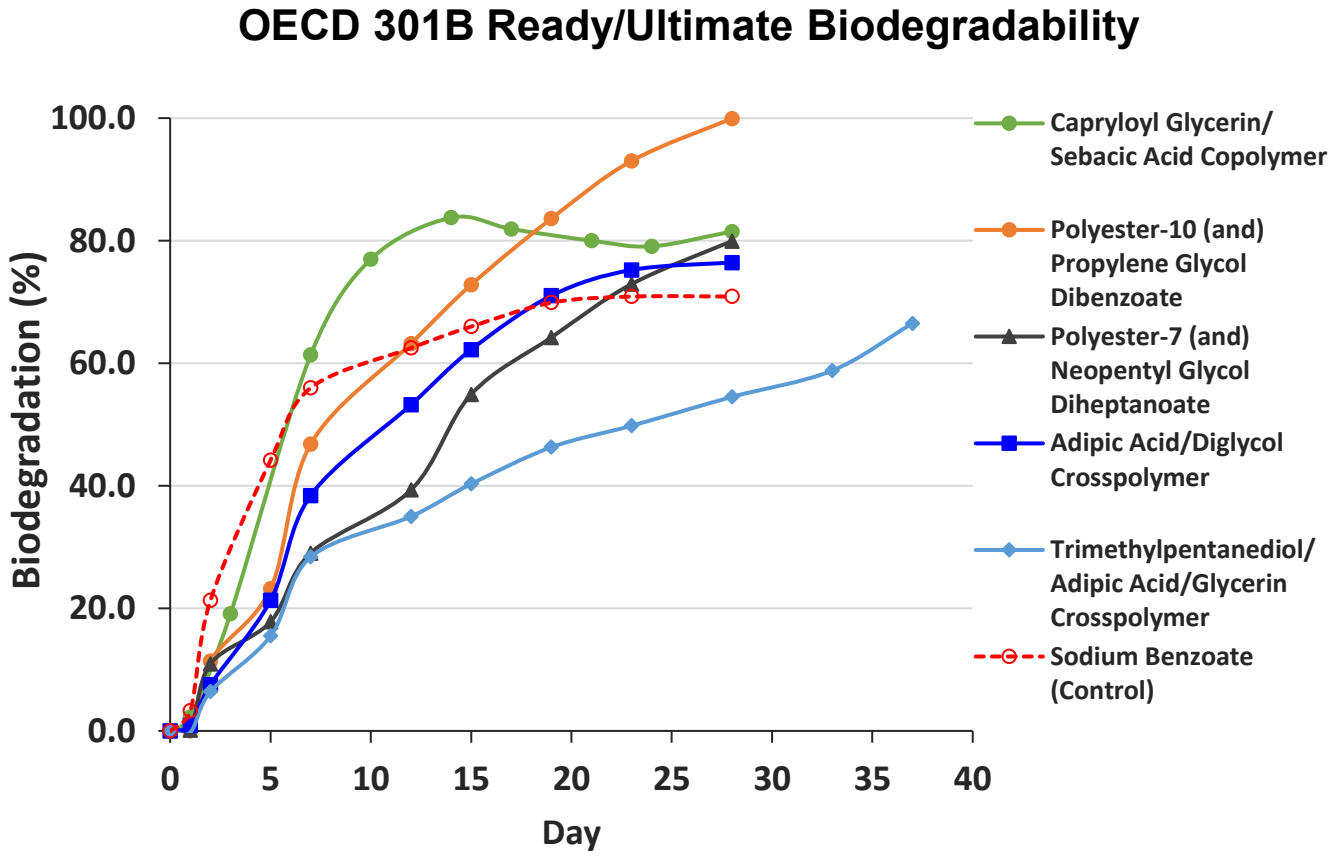
Bio-absorbable Sutures

Biodegradable Cutlery

Most polyester film formers and emollients are viscous liquids:

Biodegradability of INOLEX polyester film formers

INCI Name	Biodegradation (% at 28 d)	OECD Biodegradability Classification
Polyester-10 (and) Propylene Glycol Dibenzoate	99.9	Ready
Capryloyl Glycerin/ Sebacic Acid Copolymer	81.5	Ready
Polyester-7 (and) Neopentyl Glycol Diheptanoate	79.9	Ultimate
Adipic Acid/Diglycol Crosspolymer	76.4	Ready
Trimethylpentanediol/ Adipic Acid/Glycerin Crosspolymer	66.5* (at 37 d)	Ultimate



- Backbones with methyl branching biodegrade at slower rate
- Solubilization in ester emollients improves polymer biodegradability

Conclusion

- Castor seed oil demonstrates remarkable versatility as a feedstock for manufacturing sustainable cosmetic ingredients
- Pairing castor-derived building blocks with understanding of structure-property-performance relationships enables the development of advanced ingredients from classic natural chemistry
- Castor will play an important role as market demands continue to drive innovation in high-performance biodegradable ingredients from diverse biobased sources

Care to learn more?

Feel free to contact us!

Julia Benson
Technical Account Manager, UK
jbenson@inolex.com

Mark Evans
Commercial Director, Europe
mevans@inolex.com

Mike Fevola
Vice President, Head of R&D
mfevola@inolex.com