Greener Solutions x L'Oreal x DTSC

# Non-petroleum Based Alternatives for Nail Polish Formulations

Fall 2022

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# Meet the team

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# Presentation Overview

**Background**

- The Problem
- Challenge Statement
- Worker Exposure
- Health Performance of Existing Methods

**Performance Criteria**

- Component Functions
- Target Properties of ideal nail polish

**Our Strategies**

- Zein-based formulation
- Water-Based Solvents
- Drop-In Plasticizer Alternative

**Recommendations**

- Challenge Statement
- Worker Exposure
- Health Performance of Existing Methods

# Background

# Nail salon workers are routinely exposed to toxic chemicals

NEWS ANALYSIS | ECONOMY & LABOR

**Nail Salon Workers Face Respiratory Illness and Cancer Risks, Study Shows**

The New York Times

*Perfect Nails, Poisoned Workers*

The Current

**Nail salon workers exposed to high levels of toxic chemicals, new study reveals**

Colorado nail salon workers face chronic air pollution, elevated cancer risk

Toxic products in California nail salons under renewed scrutiny

ENVIRONMENTAL HEALTH AND SAFETY

**Toxic chemicals threaten beauty care workforce with adverse health effects**

# The Challenge: Safer, non-petroleum based nail polish formulations

## Partners

L'Oréal & the Department of Toxic Substances Control (DTSC)

## Goals

- Identify a range of non-petroleum based alternatives to existing solvents that achieve comparable technical performance
- Consider solvents, plasticizers, and film-formers that can be synthesized without petroleum products, or safer alternatives

L'ORÉAL

DTSC Department of Toxic Substances Control

# There are 3 key components of nail polish formulation

| Component | Function in formula | Current chemicals |
|---|---|---|
| **Film-former** | Binds components together<br><br>Main component in formulation | - Nitrocellulose |
| **Solvent** | Dissolves solutes<br><br>Lowers the viscosity of final formulation | - Toluene<br>- Butyl acetate<br>- Ethyl acetate |
| **Plasticizer** | Increase flexibility by softening the polymer (film former) | - Dibutyl phthalate<br>- Triphenyl Phosphate (TPhP)<br>- Di(ethylhexyl) terephthalate (DEHT)<br>- Diisononyl hexahydrophthalate (DINCH)<br>- Triethyl citrate<br>- Acetyl tributyl citrate |

**Red** = current primary bad actors

# Nail salon workers experience adverse health outcomes from workplace exposures

**Emissions**

Toluene | Triphenyl Phosphate | Dibutyl Phthalate

**Exposure**

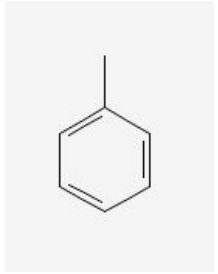
Poor Ventilation

**Nail Salon Workers**

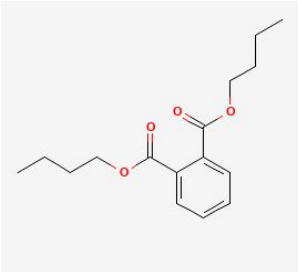
Long Hours + Chronic Exposure

**Outcomes**

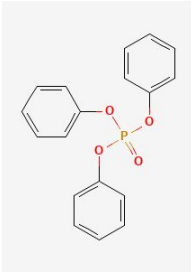
Cancer | Reproductive +Developmental Toxicity | Potential Endocrine Disruption



Toluene



Dibutyl Phthalate



Triphenyl Phosphate

# Primary bad actors are hazardous to human health

| | Carcinogenicity | Genotoxicity/ Mutagenicity | **Reproductive Toxicity** | **Developmental Toxicity** | **Endocrine Activity** | Systemic Toxicity | |
|---|---|---|---|---|---|---|---|
| **Solvent** | | | | | | acute | chronic |
| **Toluene** | L | L | H | H | H - M | M | M |
| **Plasticizer** | | | | | | | |
| **Dibutyl Phthalate** | M | L | H | H | H | L | L |
| **Triphenyl Phosphate** | M | L | L | L | M | L | M |

Data Gap | Very Low Hazard | Low Hazard | Medium Hazard | High Hazard | Very High Hazard

Sources: IARC, Prop-65, EU GHS, Pharos

# Primary bad actors are hazardous to human health

| | Carcinogenicity | Genotoxicity/ Mutagenicity | **Reproductive Toxicity** | **Developmental Toxicity** | **Endocrine Activity** | Systemic Toxicity | |
|---|---|---|---|---|---|---|---|
| **Solvent** | | | | | | acute | chronic |
| **Toluene** | L | L | H | H | H - M | M | M |
| **Plasticizer** | | | | | | | |
| **Dibutyl Phthalate** | M | L | H | H | H | L | L |
| **Triphenyl Phosphate** | M | L | L | L | M | L | M |

Data Gap | Very Low Hazard | Low Hazard | Medium Hazard | High Hazard | Very High Hazard

Sources: IARC, Prop-65, EU GHS, Pharos

# Secondary bad actors are “safer” than primary bad actors

| Plasticizer | Carcinogenicity | Develop/ Reproduct Tox | Genotoxicity/ Mutagenicity | Skin/Eye Irritation | Endocrine Activity |
|---|---|---|---|---|---|
| **Di(ethylhexyl) terephthalate** (DEHT) | L | L | L | L | DG |
| **Diisononyl hexahydrophthalate** (DINCH) | L | L | L | L | M |

| Solvent | Carcinogenicity | Develop/ Reproduct Tox | Acute/Systemic Toxicity | Skin/Eye Irritation | Endocrine Activity | Neurotoxicity |
|---|---|---|---|---|---|---|
| **Butyl Acetate** | L | M-L | M | H | DG | M-L |
| **Ethyl Acetate** | L | M-L | M | H | DG | M |

Data Gap | Very Low Hazard | Low Hazard | Medium Hazard | High Hazard | Very High Hazard

References: ECHA, GHS Japan, GHS Korea, Pharos

# Performance Criteria

# Technical specifications for nail polish formulation


- Excellent film forming properties
- Good adhesion
- Good shine properties
- Good mechanical properties
- Easy removal with non-acetone removers

| Property | Goal / Metric |
|---|---|
| Film forming | At room temperature |
| Hardness | Persoz Hardness between 50-70 oscillations |
| pH | 4-8 |
| Adhesion | > 4 for ASTM standard cross hatch tape test |
| Gloss | > 60 GU (gloss units) on Byk Gardner gloss meter |

Source: L'Oreal

# Performance criteria for each component

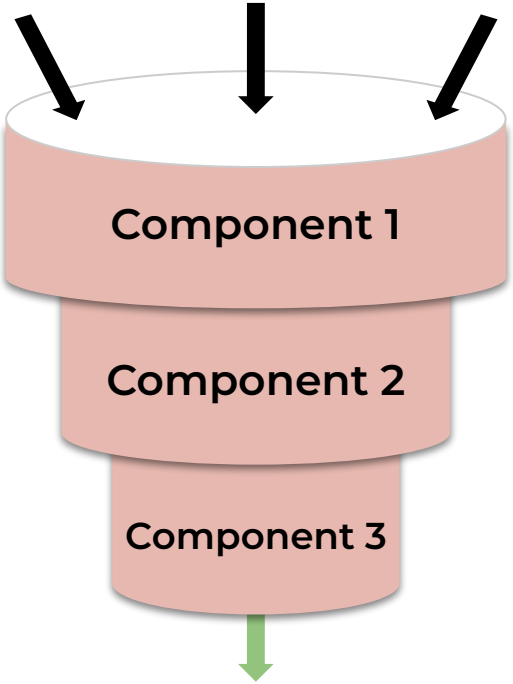
| Component | Function in formula | Max amount in % weight of component in formulation | Target Properties |
|---|---|---|---|
| **Film-former** | Binds components together when dried and thickens formulation<br><br>Main component in formulation | 50% | - Forms a film at room temperature (between 68-74 degrees Fahrenheit) |
| **Solvent** | Dissolves solutes<br><br>Lowers the viscosity of final formulation | 90% | - Low volatility (low vapor pressure)<br>- Ability to dissolve film-former and plasticizer |
| **Plasticizer** | Increase flexibility by softening the polymer (film-former) | 15% | - Molecular weight based on compatibility with film-former |

*All components should also be non-petroleum based and vegan*

Sources: L'Oreal, Development of a nail polish with minerals as caring ingredients

# Our Strategies

# 3-tiered approach to building out safer formulations




**Alternative Formulation**

Zein as a **Film-former**

Water as a **Solvent**

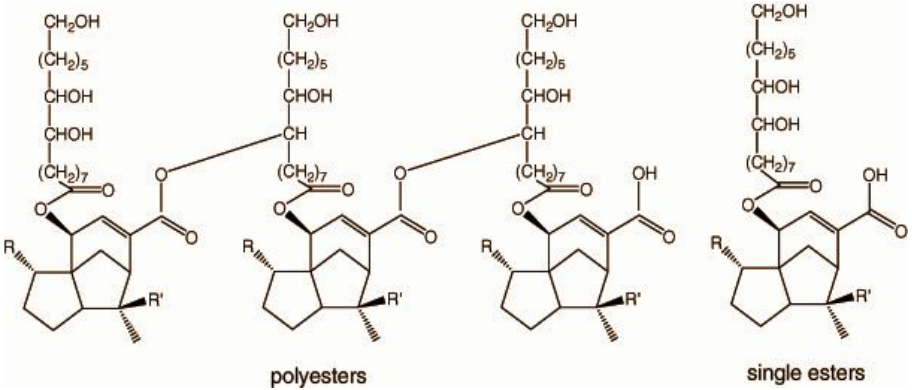
Bio-based **Plasticizer**

# Our 3 strategies target each major component of nail polish formulation

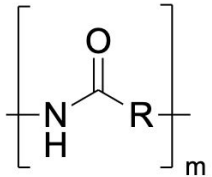
1. Building Out a Formulation from Zein as a **Film-former**
2. Water as a **Solvent** Alternative to Toluene
3. Bio-based **Plasticizer** Drop-in Replacements

# **Strategy 1** Building Out a Formulation from Zein as a Film-former

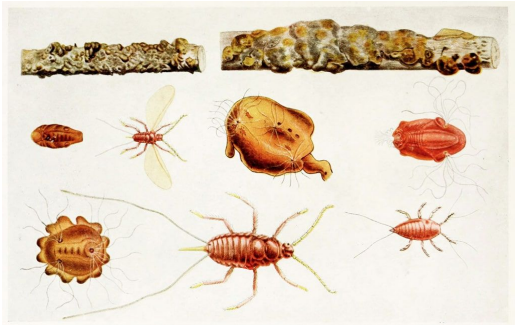
# Inspiration: Zein emulates properties of the natural resin shellac




Chemical structure of shellac.



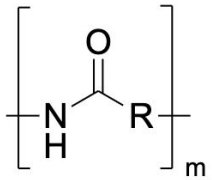
Zein monomeric unit.



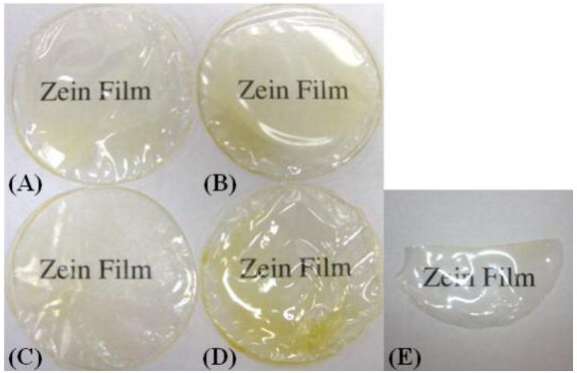
*Laccifer lacca* (aka *Tachardia lacca*).

Sample shellac colors.

# Zein is hydrophobic, vegan, and biodegradable




Zein monomeric unit.




Zein films from different processes.

| Chemical Properties | Additional Properties of Zein |
|---|---|
| • High proportion of non-polar amino acids (leucine, alanine, proline)<br>• Hydrophobic (poor water solubility, alcohol-soluble)<br>• Film forms through hydrogen and limited disulfide bonds between zein chains | • Zein films are brittle - need plasticizers to make them soft and “permanently flexible”<br>• Low water vapor permeability<br>• High fatty acid-binding capacity<br>• Vegan<br>• Biodegradable |

Natural Polymers: Volume 1: Chapter 10
Anderson et al., 2022

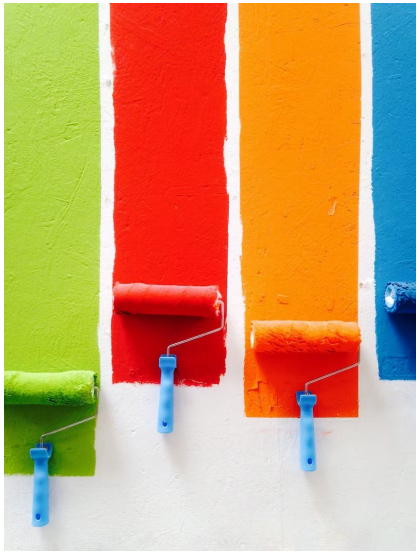
# Plasticizer was selected based on compatibility with zein and existing formulations

### *Existing Formulations*

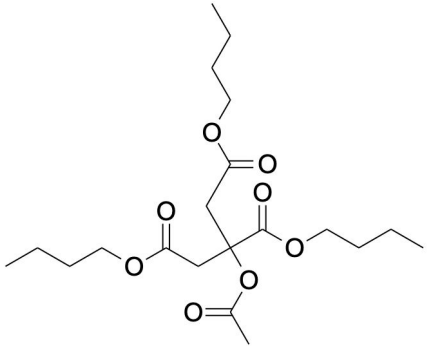
Acetyl tributyl citrate is already used in ~7% of nail polish formulations as a plasticizer

### *Zein Compatibility*

(Shi. K et al., 2012) found zein mixed with 10% tributyl citrate can achieve an ideal level of flexibility and toughness in high humidity and water



**Plasticizer**



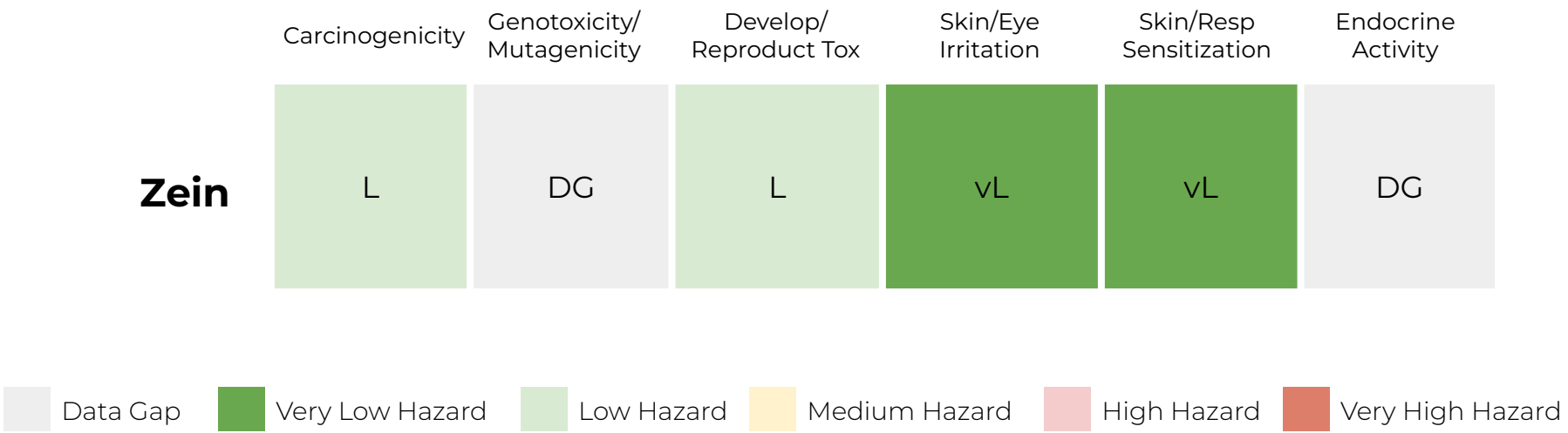
***Acetyl Tributyl Citrate***

# Solvent selection was driven by the GSK Solvent Selection Guide and zein extraction methods

| Classification | Solvent Name | CAS Number | Composite Colour‡ | Boiling Point (°C) | Incineration | Recycling | Biotreatment | VOC Emissions | Aquatic Impact | Air Impact | Health Hazard | Exposure potential | Flammability & Explosion | Reactivity & Stability | Life Cycle Analysis† |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alcohols | 1-Heptanol | 111-70-6 | | 178 | 9 | 8 | 10 | 9 | 8 | 4 | 10 | 7 | 9 | 10 | |
| | Ethylene glycol | 107-21-1 | | 197 | 4 | 5 | 5 | 10 | 10 | 8 | 7 | 10 | 10 | 10 | 9 |
| | 1-Octanol | 111-87-5 | | 195 | 9 | 7 | 8 | 10 | 5 | 4 | 7 | 10 | 9 | 10 | |
| | 1-Butanol | 71-36-3 | | 118 | 6 | 7 | 5 | 8 | 9 | 3 | 7 | 7 | 8 | 9 | 5 |
| | 1-Propanol | 71-23-8 | | 97 | 5 | 3 | 3 | 6 | 10 | 4 | 10 | 7 | 8 | 10 | 7 |
| | Ethanol | 64-17-5 | | 78 | 5 | 5 | 3 | 4 | 9 | 5 | 10 | 8 | 6 | 10 | |
| | 2-Propanol | 67-63-0 | | 82 | 5 | 5 | 3 | 5 | 8 | 7 | 10 | 6 | 6 | 8 | 4 |
| | *t*-Butanol | 75-65-0 | | 82 | 5 | 5 | 3 | 5 | 9 | 7 | 7 | 5 | 6 | 10 | 8 |
| | IMS (ethanol, denatured) | 64-17-5 | | 78 | 5 | 5 | 3 | 5 | 9 | 5 | 4 | 7 | 6 | 10 | |
| | Methanol | 67-56-1 | | 65 | 4 | 7 | 3 | 3 | 10 | 7 | 4 | 6 | 5 | 10 | 9 |

- (Li et al., 2012) zein has been shown to dissolve well in 70% ethanol and commercially extracted using 88% isopropanol
- Both solvents can be produced in a bio-based manner

# Zein has low toxicity endpoints




Sources: EPA, PubChem, IARC

# Acetyl tributyl citrate shows similar hazard endpoints to primary bad actor plasticizers

| | Carcinogenicity | Genotoxicity/ Mutagenicity | Develop/ Reproduct Tox | Skin/Eye Irritation | Endocrine Activity |
|---|---|---|---|---|---|
| **Acetyl Tributyl Citrate** | L | vL | L | vL-M | M |

| **Current Plasticizer**** | Carcinogenicity | Genotoxicity/ Mutagenicity | Develop/ Reproduct Tox | Skin/Eye Irritation | Endocrine Activity |
|---|---|---|---|---|---|
| **Di(ethylhexyl) terephthalate** (DEHT) | L | L | L | L | DG |
| **Diisononyl hexahydrophthalate** (DINCH) | L | L | L | L | M |

***both are phthalates*

Data Gap | Very Low Hazard | Low Hazard | Medium Hazard | High Hazard | Very High Hazard

Sources EPA; PubChem; IARC; Johnson, 2002; Sheikh and Beg, 2019

# Ethanol and isopropanol are less hazardous than current “safe” solvents

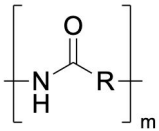
| | Carcinogenicity | Genotoxicity/ Mutagenicity | Develop/ Reproduct Tox | Skin/Eye Irritation | Endocrine Activity |
|---|---|---|---|---|---|
| **Ethanol** | L | L | M-L | H-L | DG |
| **Isopropanol** | L | L | M | H-M | DG |
| **Current Solvents** | | | | | |
| **Butyl Acetate** | L | M-L | M | H | DG |
| **Ethyl Acetate** | L | M-L | M | H | DG |

Data Gap | Very Low Hazard | Low Hazard | Medium Hazard | High Hazard | Very High Hazard

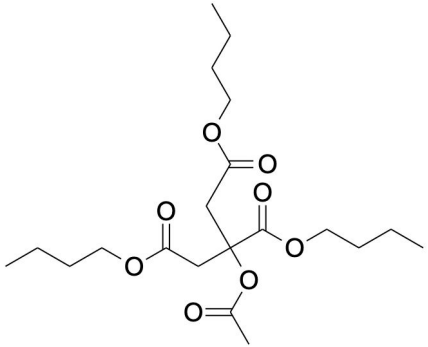
Sources: EPA, PubChem, IARC

# Sample zein-based formulation shows promising technical performance with room for improvement

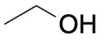
**Film-former** → **Plasticizer** → **Solvent**



*Zein*



*Acetyl Tributyl Citrate*



*Ethanol*

*Isopropanol*

## Future Directions

**Improving current formulation**

- Solvent mixtures (ethanol & isopropanol)
- Antioxidants (carotenoids, vitamin E/C, ...)
- Blue-colored chemical to neutralize yellow

**Developing other formulations**

- Different solubility guides (Pfizer, Sanofi, ...)
- Solubility parameters (Hansen, Hildebrand, ...)
- Other hydrophobic solvents (non-alcohols)

# **Strategy 2** Water as a Solvent Alternative to Toluene

# Strategy 2: Water as a solvent alternative

| Component | Function in formula | Max amount in % weight of component in formulation | Current Chemicals |
|---|---|---|---|
| **Film-former** | Binds components together when dried and thickens formulation<br><br>Main component in formulation | 50% | - Nitrocellulose |
| **Solvent** | Dissolves solutes<br><br>Lowers the viscosity of final formulation | 90% | - Toluene<br>- Butyl acetate<br>- Ethyl acetate |
| **Plasticizer** | Increase flexibility by softening the polymer (film-former) | 15% | - Dibutyl phthalate<br>- Triphenyl Phosphate (TPhP)<br>- Di(ethylhexyl) terephthalate (DEHT)<br>- Diisononyl hexahydrophthalate (DINCH)<br>- Triethyl citrate<br>- Acetyl tributyl citrate |

Red = current primary bad actors

# Water has no known hazards

| | Carcinogenicity/ Mutagenicity | Develop/ Reproduct Tox | Endocrine Activity | Skin/Eye Irritation | Acute/Systemic Toxicity | Neurotoxicity |
|---|---|---|---|---|---|---|
| Toluene | L | H | H-M | H | M | M-L |
| Butyl Acetate | L | M-L | DG | H | M | M-L |
| Ethyl Acetate | L | M-L | DG | H | M | M |
| **Water** | L | L | L | L | L | L |

Data Gap | Very Low Hazard | Low Hazard | Medium Hazard | High Hazard | Very High Hazard

Sources: IARC, Prop-65, EU GHS, New Zealand GHS, Pharos, EWG Skin Deep, REACH

# Many water-based formulations use acrylates copolymers as film-formers

| Brand | Film-former | Plasticizer | Full Ingredient List |
|---|---|---|---|
| Acquarella | Acrylates Copolymer | N/A | Aqua, Styrene Acrylates Copolymer, Acrylates Copolymer. Pigments |
| Honeybee Gardens No Nasties (peelable) | Acrylates Copolymer | N/A | Water (aqua), acrylates copolymer. Pigments |
| Sophi Piggy Paint | Acrylates Copolymers | Melia Azadirachta (Neem Oil) | Aqua, Acrylates Copolymers, Melia Azadirachta (Neem Oil). Pigments. |
| Keeki Pure and Simple | Acrylates Copolymers | glycol ethers (unspecified) | Water, acrylate copolymer emulsion, glycol ethers. Pigments. |
| Rosajou | PEG-150/Decyl Alcohol/SDMI Copolymer Polyurethane-61 | PPG-2 Methyl Ether Polyurethane-61 | Water, Polyurethane-61, Silica, PPG-2 Methyl Ether, Phenoxyethanol, Sodium Dehydroacetate, Propylene Glycol, PEG-150/Decyl Alcohol/SDMI Copolymer, PPG-30 Butyl Ether, Ethylhexyglycerin, Bentonite, Ammonium Hydroxide, Silica Dimethyl Silylate, Tocopherol |
| Miniso | Polyurethane-1 | propylene glycol | Polyurethane-1, water, propylene glycol, stearalkonium bentonite |

Source: My List of Water Based, Peelable & Odourless Non-Toxic Nail Polish

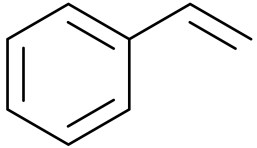
# Syntran 5620 CG is a film-former developed for water-based nail enamels

***Styrene/acrylates/ ammonium methacrylate copolymers are made up of 3 components***

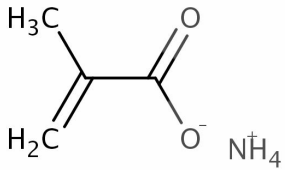
Syntran 5620 CG* is a specific version of this copolymer:

- 42% solids
- Miscible with water
- pH of 7-8
- Flammable at >120°C

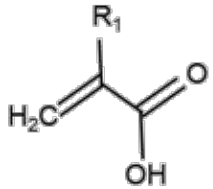
**Syntran 5620 CG is an updated version of Syntran PC 5620 without the methylisothiazolinone (MIT) preservative*



Styrene

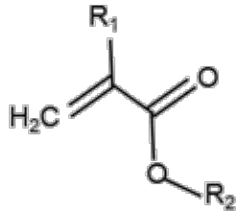



Ammonium methacrylate



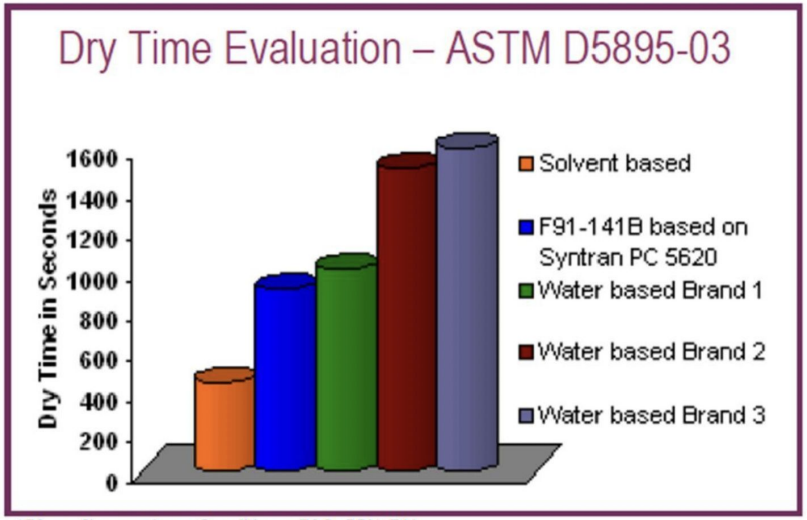

Acrylic acid ($R_1$ = H)
OR
Methacrylic acid
($R_1$ = $CH_3$)

OR

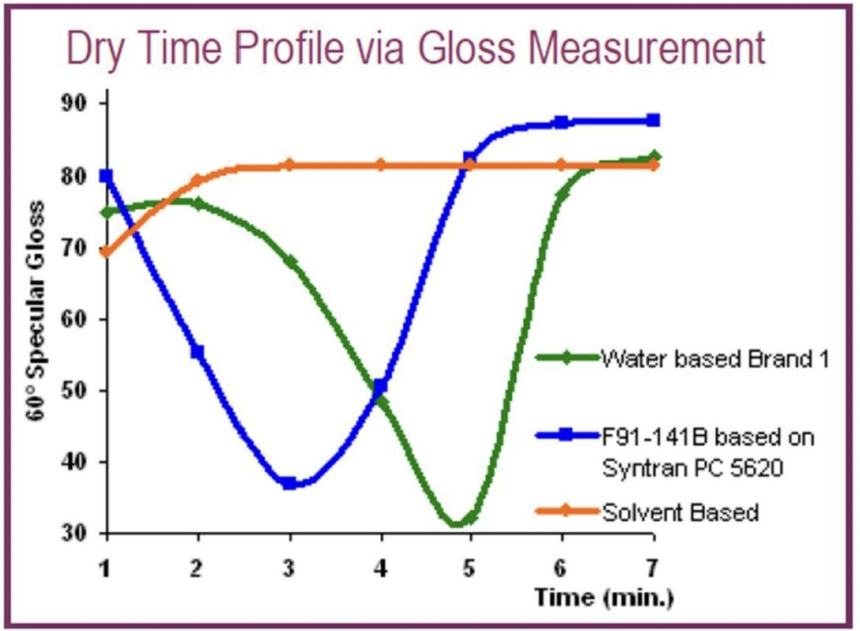



Acrylate ester ($R_1$ = H)
OR
Methacrylate ester
($R_1$ = $CH_3$)

# Water-based formulations are slower drying than their solvent counterparts




150µm film on glass; Conditions: 70C, 55% RH




Wet film applied on Leneta cards (black portion), rubbed with gauze at 1min intervals, average of 3 gloss readings; Conditions: 71C, 53% RH.

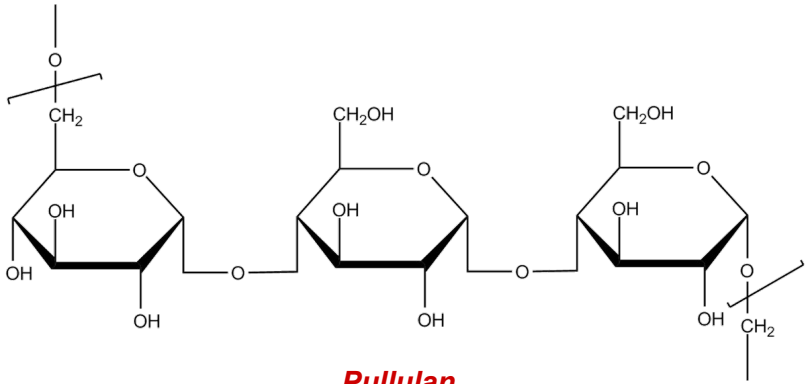
ZSCHIMMER & SCHWARZ INTERPOLYMER Creative Polymer Solutions

# Acrylates copolymers have concerning health endpoints

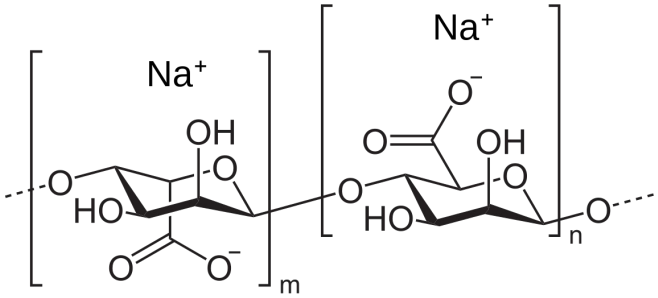
| | Styrene | Methacrylate ester | Ammonium methacrylate copolymers |
|---|---|---|---|
| Acute Exposure | - Mucous membrane & Eye irritant<br>- Gastrointestinal effects | - Skin, eye, and nose irritant | - Skin and eye irritant |
| Chronic Exposure | - Central nervous system<br>- Hearing loss<br>- Peripheral neuropathy | - Development of skin allergy<br>- Itching<br>- Skin rash | - Skin and eye irritant |
| Reproductive/ Developmental Toxicity | - No increase in developmental effects<br>- Increase in spontaneous abortions<br>- Decrease in sperm concentration | Data Gap | Data Gap |
| Carcinogenicity | - Group 2B | - Not classifiable to cause cancer | - Not classifiable to cause cancer |

References: IARC, EPA, ASTDR, ECHA

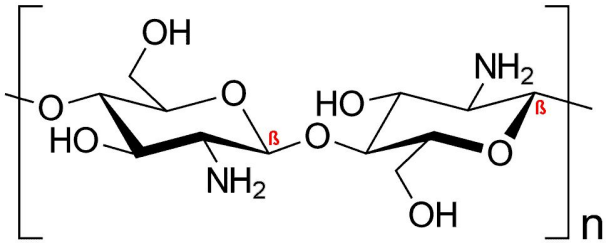
# Various natural film-formers also dissolve well in water



*Pullulan*



*Alginates (e.g. sodium alginate)*



*Chitosan*

# Final considerations for water-Based formulations

**Pros**

- Eliminates bad actor chemicals
- Odorless
- Non-flammable

**Solutions**

- Instructions to apply 2-3 thin coats
- Allow 15 mins to dry between coats
- Let cure for 6+ hours overnight
- Antibacterial agents

**Cons**

- Dries top-down
- Long dry time
- Absorbs water
- Bacterial growth

**Future Directions**

- **Less toxic film-formers**
- **Solubility of plasticizers with proposed Syntran 5620 CG**
- **Properties of proposed natural water-soluble film-former**
- **Applicability of water-based properties of cosmetics to nails**

# **Strategy 3** Bio-based Plasticizer Drop-in Replacements

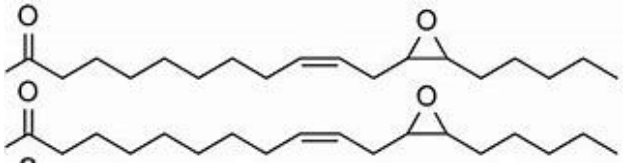
# Strategy 3: Drop-in plasticizer alternatives

| Component | Function in formula | Max amount in % weight of component in formulation | Current Chemicals |
|---|---|---|---|
| **Film-former** | Binds components together when dried and thickens formulation<br><br>Main component in formulation | 50% | - Nitrocellulose |
| **Solvent** | Dissolves solutes<br><br>Lowers the viscosity of final formulation | 90% | - Toluene<br>- Butyl acetate<br>- Ethyl acetate |
| **Plasticizer** | Increase flexibility by softening the polymer (film-former) | 15% | - Dibutyl phthalate<br>- Triphenyl Phosphate (TPhP)<br>- Di(ethylhexyl) terephthalate (DEHT)<br>- Diisononyl hexahydrophthalate (DINCH)<br>- Triethyl citrate<br>- Acetyl tributyl citrate |

Red = current primary bad actors

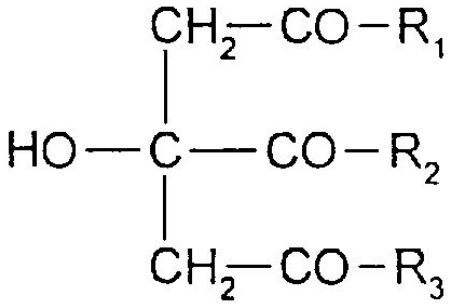
# Many companies are developing alternative plasticizers to shift away from phthalates

## Epoxidized oils (Vernonia Oils)

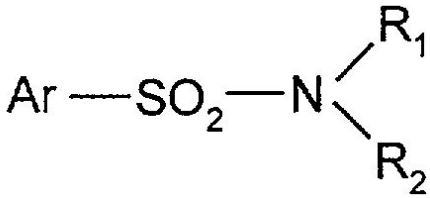


*Vernonia galamensis (Ironweed)*

## Cross-linked polyesters




## Sulfonamides




*Sources:*
*Patents: FR2785531; 5,578,297; 5,882,636; US 8,187,576 B2*

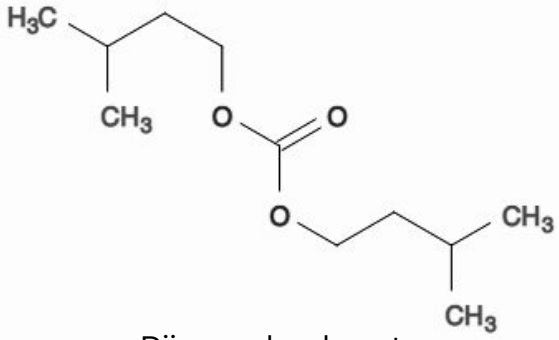
# Natural carbonates are plasticizers that can be prepared in bio-based manners

Generic carbonates:

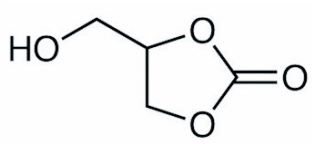
$R_1OCOOR_2$

Where:

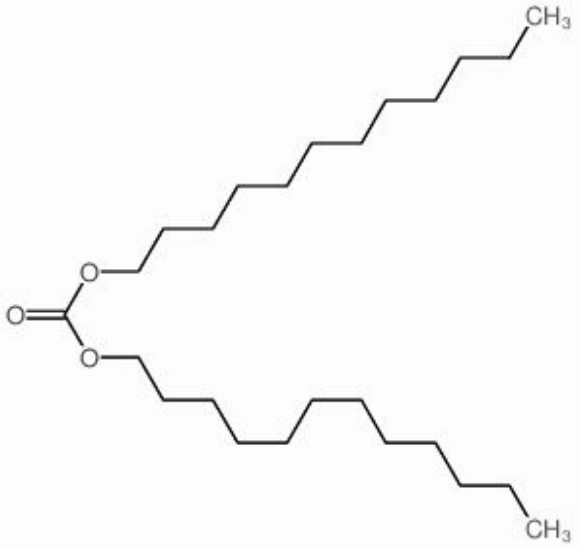
1. $R_1$ and $R_2$ are equivalent
2. $R_1$ and $R_2$ form an alkyl chain with 2 or 3 carbon atoms and one or more hydroxy or hydroxy($C_1$-$C_3$)alkyl groups




Diisoamyl carbonate




Glycerol carbonate

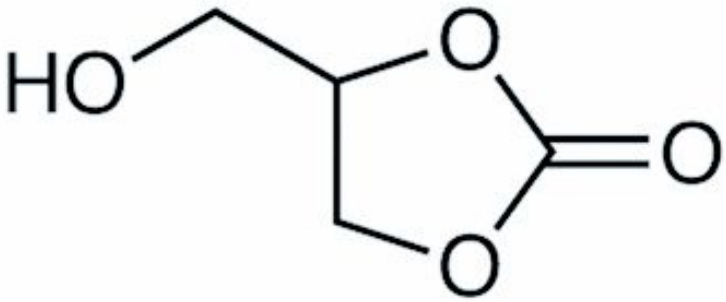



Dilauryl carbonate

Source: Patent No.: US 8,187,576 B2

# Glycerol carbonate has good plasticizing properties for nail polish

- Chemically stable
- **Non-flammable** (Flash Point >204°C)
- **Water-soluble**
- Biodegradable
- Low volatility (Boiling Point 110–115°C at 0.1 mmHg)
- **High renewable content** (76 - 100% depending on synthesis route)

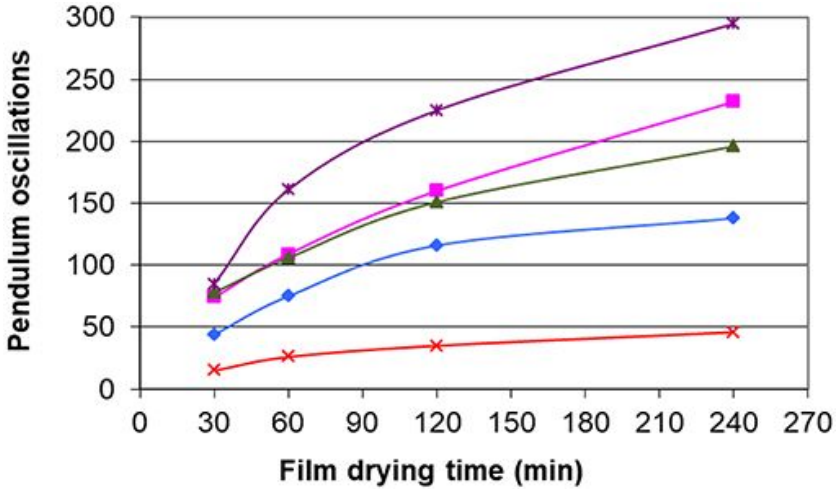



Glycerol carbonate

Sources: Patent No.: US 8,187,576 B2
Clemson, 2003

# Glycerol carbonate has better plasticizing properties than the commercial plasticizer

## Effect of the plasticizers on the Persoz hardness




✘ no plasticizer, ■ diisoamyl carbonate, ▲ dilauryl carbonate, ◆ acetyl tributyl citrate, ● glycerol carbonate

## Formulation

| Ingredient | % Composition |
|---|---|
| Solvents* | 59.1 |
| Nitrocellulose | 17.9 |
| Polyester resin | 13.3 |
| Plasticizer | 9.9 |

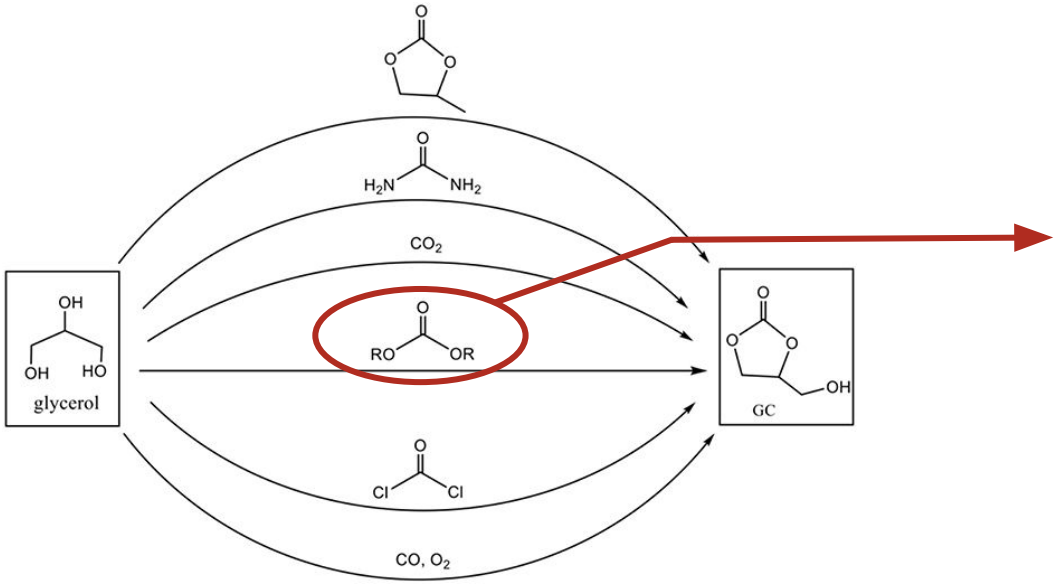
**mixture of ethyl acetate, butyl acetate, and isopropanol*

## Results

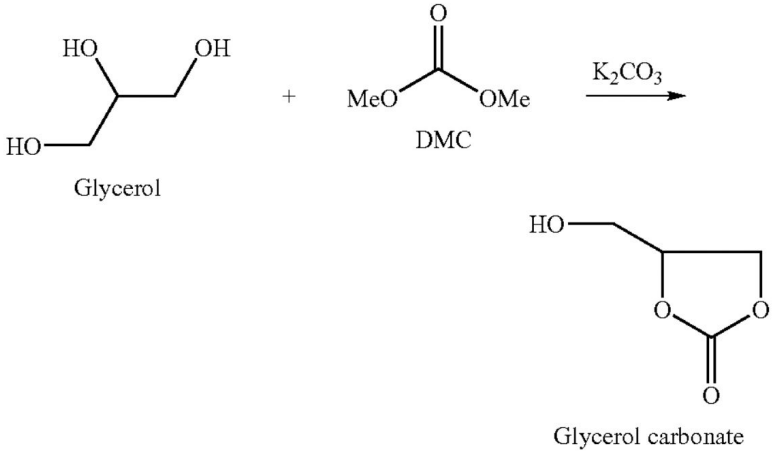
- Moderate plasticizing effect for dilauryl carbonate and diisoamyl carbonate
- Glycerol carbonate had better plasticizing properties than the commercial plasticizer

Source: de Caro et al., 2019

# Glycerol carbonates can be synthesized in a variety of ways



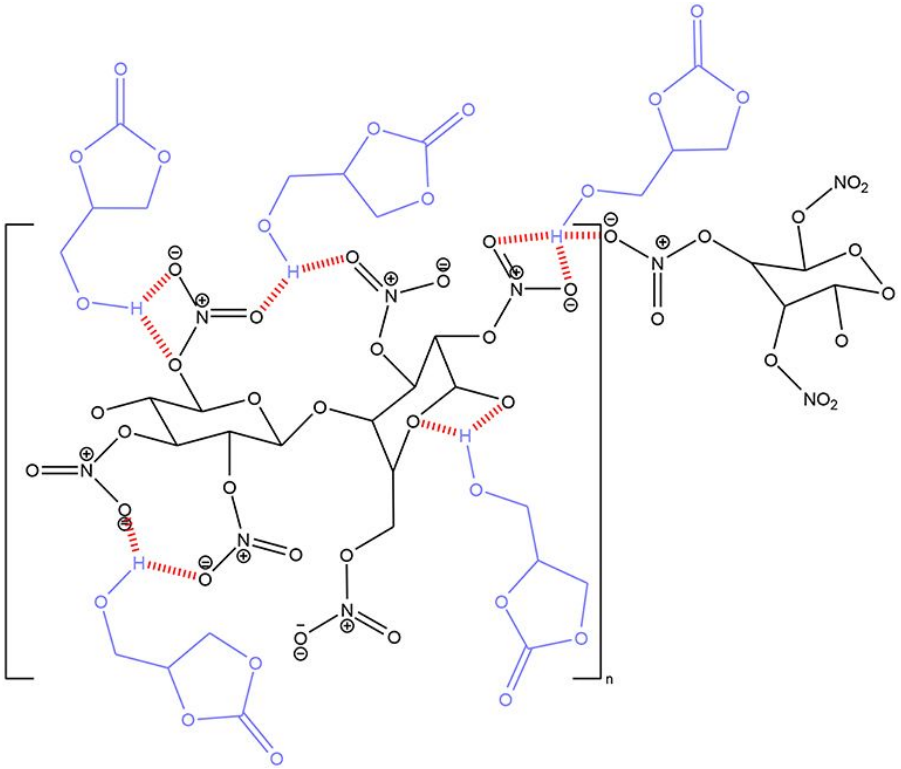

**Different conversion routes for synthesis of glycerol carbonate.**




**Synthesis of glycerol carbonate from dimethylcarbonate (DMC) and glycerol (an alcohol).**

Source: de Caro et al., 2019

# Glycerol carbonates interact strongly with nitrocellulose



**Proposed arrangement of glycerol carbonate molecules within nitrocellulose chains.**

- Hydrogen bonds between hydroxyl groups of glycerol carbonate and $NO_2$ groups of nitrocellulose
- Large and well-distributed free volume between nitrocellulose chains → high plasticizing effect
- Glycerol carbonate can be reduced below 10% to meet specifications of nail polish

de Caro et al., 2019

# The hazard assessment of plasticizer alternatives indicates notable data gaps

| Plasticizer : | Carcinogenicity/ Mutagenicity | Develop/ Reproductive Tox | Skin/Resp Sensitization | Skin/Eye Irritation | Endocrine Activity | Systemic Toxicity |
|---|---|---|---|---|---|---|
| **Diisoamyl carbonate** 2050-95-5 | DG | M | DG | DG | DG | DG |
| **Dilauryl carbonate** 6627-45-8 | DG | DG | DG | vH | DG | DG |
| **Glycerol carbonate** 96-49-1 | DG | DG | DG | vH | DG | M |
| **Acetyl tributyl citrate** 77-90-7 | L-vL | L | vL | M-vL | M | DG |

*None of these plasticizers are considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200)*

Data Gap | Very Low Hazard | Low Hazard | Medium Hazard | High Hazard | Very High Hazard

Sources: 29 CFR 1910.1200, Pharos, Johnson, Sheikh and Beg, 2019, EU GHS

# Drop-in bio-based plasticizers show strong technical performance but lack information regarding health endpoints

## Technical Performance

- Natural carbonates can be synthesized via multiple pathways
- Glycerol carbonate outperforms ATBC in terms of plasticizing effects

### Future Directions

- Other glycerol esters (glycerol triacetate, glyceroltrioctanoate, glyceroltribenzoate, ...)
- Related classes to carbonates (diols, glycols, ...)
- Non-glycerol related substitutes (adipates, pentaerythrityltetrabenzoate, 2,2,4-trimethyl-1,3-pentanedioldisobutyrate, ...)

## Health Endpoints

- ATBC outperforms glycerol carbonate
- Glycerol carbonate (GC)
  - Systemic toxicity
  - Acute Toxicity
- GC Data Gaps
  - Predictive tools suggests significant toxicity
  - Cramer Class III (ToxTree)

### Future Directions

- Preference for ATBC as used in Strategy 1

# Recommendations

# Comparison of proposed strategies

| | Pros | Cons | Notes | Questions |
|---|---|---|---|---|
| **Zein-based formulation** | • Hydrophobic<br>• Biodegradable<br>• Flexible formulation | • Requires alcohol for removal<br>• Remains skin and eye irritant | • Includes safer solvent alternative current actors<br>• Zein has no known toxic endpoints<br>• New approach to bring to market | • Is there an antioxidant that can be used with zein to prevent the color change? |
| **Water as an alternative solvent** | • Easily removed<br>• Water = no toxic health endpoints | • Requires additive to increase hardness + reduce bacterial growth<br>• Slow dry time<br>• Difficult application instructions | • Reduced need for hazard communication - safer for workers<br>• Inexpensive<br>• Soy-based remover<br>• Existing formulations already on market | • What is the ability of the formulas to suspend the pigments? Do we need an additive? |
| **Bio-based drop-in plasticizer replacement** | • Developed in many ways<br>• Well-researched compatibility between formulation components | • Many data gaps regarding health endpoints | • This method will require additional testing prior to use to see interactions with other compounds | • How do we classify compounds that are both plasticizers and film formers? |

# Final recommendation: further research on zein-based formulations

➔ **Zein-based formulation has potential to achieve similar results to Shellac**

- Inexpensive, Vegan, Bio-inspired

➔ **Water-based formulations may not achieve long-lasting results**

- Customer reviews report dissatisfaction
- Additives must be considered

➔ **Consider alternative plasticizers in formulations**

- Many data gaps regarding potential plasticizer alternatives
- L'Oreal and DTSC should explore alternatives to evaluate use

**All strategies eliminate bad actors. Zein-based formulation offers a new and inexpensive approach to create vegan, clean-beauty nail polishes.**

# Thank you for joining us today

& a special thank you to our partners at L'Oreal and DTSC.


L'ORÉAL

DTSC
Department of Toxic Substances Control

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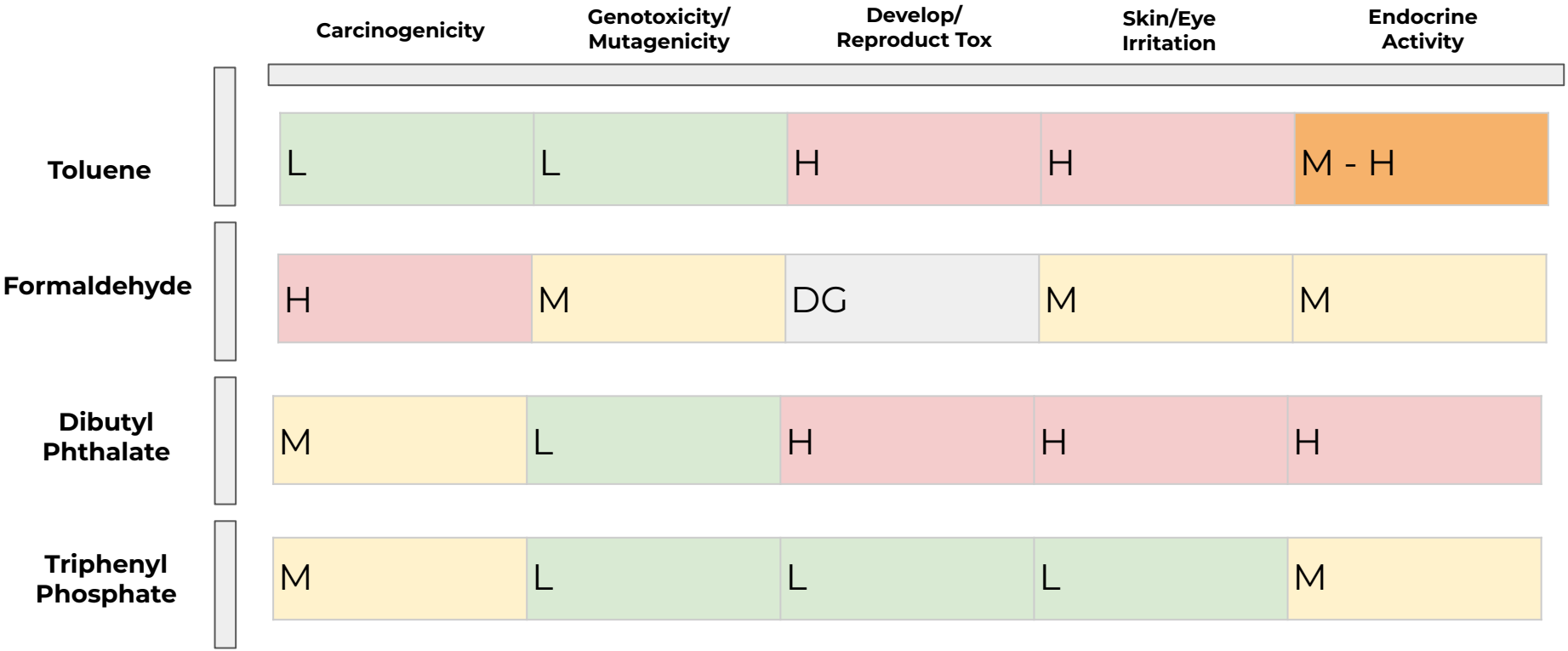
# Appendix

# How hazard assessments were conducted

- Literature
  - IARC
  - IRIS
  - European Commission: Scientific Committee on Toxicity, Ecotoxicity and the Environment
  - EPA
  - Consumer Product Safety Commission
  - PubChem
  - Agency for Toxic Substances and Disease Registry (ATSDR)
  - U.S. Department of Health and Human Services
  - CDC
- Screening tools
  - Pharos
  -

# Hazard Assessment Primary Bad Actors



# Strategy 1: Alternative Solution Hazards

| | Carcinogenicity | Genotoxicity/ Mutagenicity | Develop/ Reproduct Tox | Skin/Eye Irritation | Skin/Resp Sensitization | Endocrine Activity |
|---|---|---|---|---|---|---|
| **Zein** | L | DG | L | vL | vL | DG |
| **Acetyl Tributyl Citrate** | L | vL | L | vL-M | vL | M |
| **Ethanol** | L | L | M-L | H-L | L | DG |
| **Isopropanol** | L | L | M | H-M | M | DG |

Data Gap | Very Low Hazard | Low Hazard | Medium Hazard | High Hazard | Very High Hazard

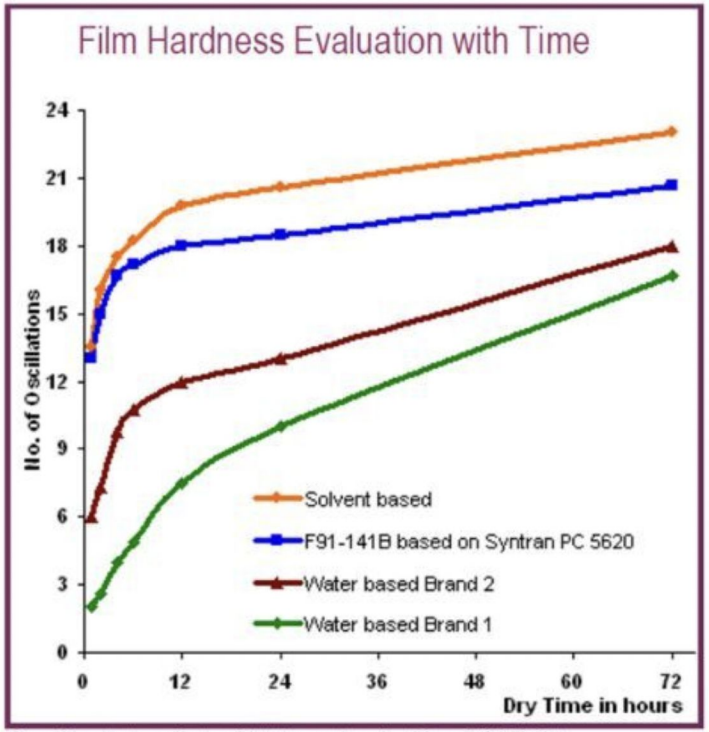
Sources: EPA, PubChem, IARC, Pharos

# Hazard Assessment of Film-formers in Existing Water-Based Formulations

| Film-former: | Carcinogenicity/ Mutagenicity | Develop/ Reproductive Tox | Skin/Resp Sensitization | Skin/Eye Irritation | Endocrine Activity | Systemic Toxicity |
|---|---|---|---|---|---|---|
| **Acrylates Copolymer** 25133-97-5 | DG | DG | DG | DG | DG | DG |
| **Acrylates Copolymer** 25035-69-2 | DG | DG | DG | DG | DG | DG |
| **Acrylates Copolymer** 25212-88-8 | DG | DG | H | DG | DG | DG |
| **PEG-150/Decyl/Alcohol/SDMI Copolymer** 193487-42-2 | L | L | DG | DG | DG | DG |

Data Gap | Very Low Hazard | Low Hazard | Medium Hazard | High Hazard | Very High Hazard

# Water-based formulations with Syntran PC 5620 showed high film hardness




Sward-Type Hardness Rocker, 6 MIL film on glass; Conditions: 71C, 57% RH.

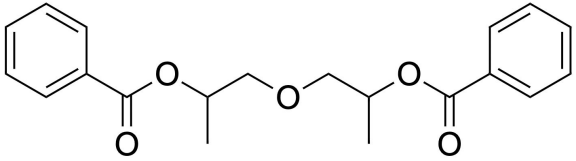
## Starting Point Formulation

**WATER-BASED ACRYLIC NAIL POLISH WITH SYNTRAN® PC 5620**
**Formulation F91-141B**

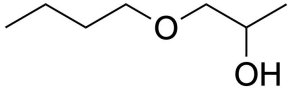
| | INCI Designation | Weight % |
|---|---|---|
| **Phase A** | | |
| **Syntran® PC 5620** | Pending | **92.00** |
| **Phase B** | | |
| Benzoflex 9-88 (Genovique) | Dipropylene glycol dibenzoate | 2.40 |
| Dowanol PnB (Dow) | Propylene glycol n-butyl ether | 4.40 |
| **Syntran® KL-219CG** | Ammonium Acrylates Copolymer | **1.20** |
| | **YIELD:** | **100.00** |

**Procedure:**
Add **Syntran®** PC 5620 to batch tank. Begin appropriate agitation. In a separate vessel, premix Phase B with appropriate agitation. Slowly add Phase B to Phase A with **constant agitation**. Stir for 30 minutes and avoid aeration.
PROPERTIES: pH: 7.0-8.0; solids: 41-43%

# Benzoflex 9-88 and Dowanol PnB can provide plasticizing properties



Benzoflex™ 9-88



DOWANOL™ PnB
Glycol Ether

| | Benzoflex™ 9-88 | DOWANOL™ PnB Glycol Ether |
|---|---|---|
| **MW (g/mol)** | 474.59 | 132.2 |
| **Water solubility (g/L) @ RT** | - | 52 |
| **Viscosity (mPa•s) @ 25°C** | 105 | 2.8 |
| **Flash point (°C)** | 182 | 63 |

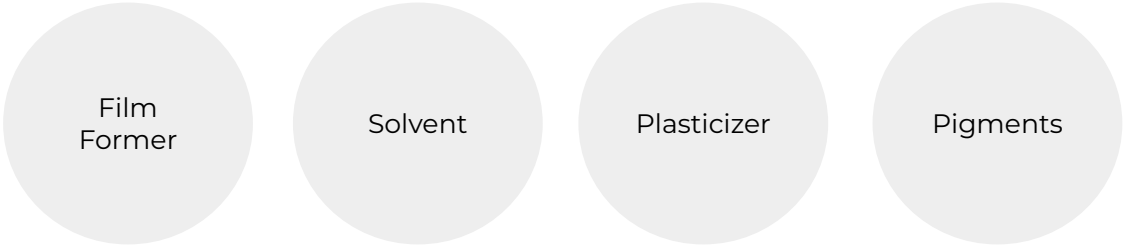
# Acrylates copolymer has high toxicity

| Film-former: | Carcinogenicity/ Mutagenicity | Develop/ Reproductive Tox | Skin/Resp Sensitization | Skin/Eye Irritation | Endocrine Activity | Systemic Toxicity |
|---|---|---|---|---|---|---|
| **Acrylates Copolymer** | L | L | L | M-L | DG | DG |
| **PEG-150/Decyl/ Alcohol/SDMI Copolymer** 193487-42-2 | L | L | DG | DG | DG | DG |

Data Gap | Very Low Hazard | Low Hazard | Medium Hazard | High Hazard | Very High Hazard

# Strategy 2: Water-based Nail Polish Formulation

## Typical Formulation




## Water-Based Alternative


### Pros

Eliminates bad actor chemicals, Odorless, Non-flammable

### Cons

Dries top-down, Long dry time, Absorbs water, Bacterial growth

### Solution

Include application instructions to apply 2-3 thin coats and allow 15 mins to dry between coats, Let cure for 6+ hours overnight

# Hazard Assessment of Plasticizers in Existing Water-Based Formulations

| Plasticizer: | Carcinogenicity/ Mutagenicity | Develop/ Reproductive Tox | Skin/Resp Sensitization | Skin/Eye Irritation | Endocrine Activity | Systemic Toxicity |
|---|---|---|---|---|---|---|
| **Neem Oil (Melia azadirachta)** 947173-77-5 | L | L | DG | DG | DG | DG |
| **PPG-2 Methyl Ether** 88917-22-0 | DG | pC | pC | pC | DG | DG |
| **Propylene glycol** 57-55-6 | L | L | L | DG | DG | M |

Data Gap | Very Low Hazard | Low Hazard | Medium Hazard | High Hazard | Very High Hazard

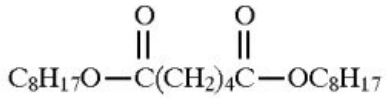
# Other Plasticizers of Natural Origin

## Plasticizer Properties

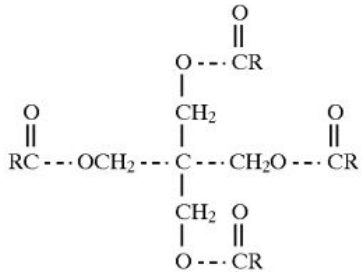
- Remain in polish film
- Flash point > 30°C

## Phthalate-free nail polish enamel composition substitutions:

*Adipates*



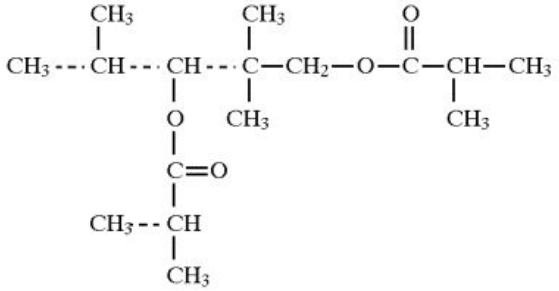
*Pentaerythrityl tetrabenzoate*



## Carbonates

- Prepared by reaction of Dimethyl Carbonate (DMC)
- Glycerol carbonate

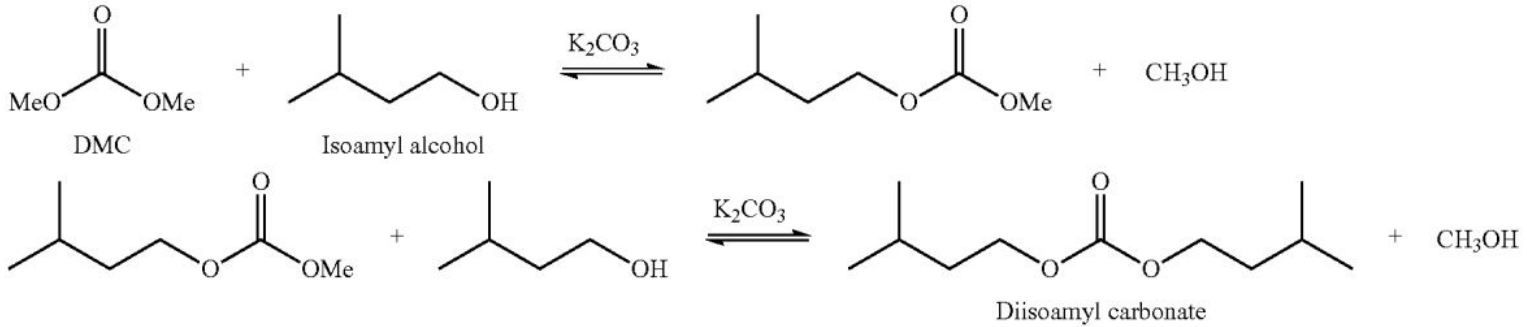
*2,2,4-trimethyl-1,3-pentanediol diisobutyrate*



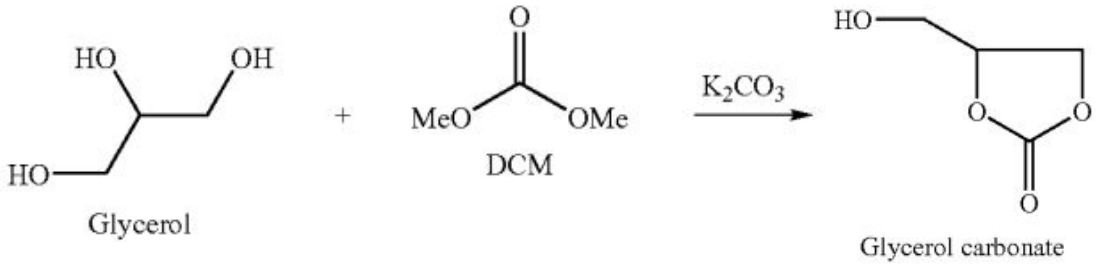
# Current Plasticizer of Natural Origin

**Dimethyl Carbonate Synthesis**

## Diisoamyl Carbonate



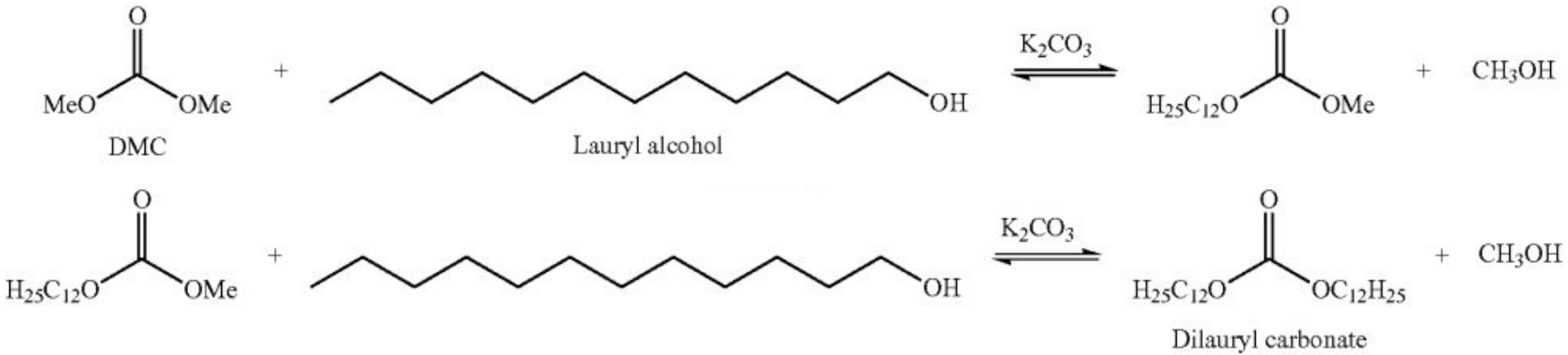

## Glycerol Carbonate



# Current Plasticizer of Natural Origin

## Dimethyl Carbonate Synthesis

### Dilauryl Carbonate



- Dimethyl carbonate transesterification base catalysis
  - Green chem
  - Catalyst: potassium carbonate ($K_2CO_3$)
- Dmc
  - Non-toxic
  - Manufactured to a clean process
  - Replaces toxic and hazardous reagents
- Synthesis of diisoamyl, dilauryl & glycerol carbonates
  - Rxn of DMC with isoamyl alcohol, dodecanol, or lauryl alcohol, and glycerol
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# Ranking Solutions - In Progress

| | Criteria 1 | Criteria 2 | Criteria 3 |
|---|---|---|---|
| **Zein-based formulation** | | | |
| **Water as an alternative solvent** | | * | |
| **Bio-based drop-in plasticizer replacement** | | | |

# Additional references not in folders

1. Measurement of Sixty-Degree Specular Gloss
2. Plasticizer of Natural Origin for Nail Polish
3. Phthalate free nail polish enamel composition
4. Nail varnish composition comprising a crosslinked polyester
5. Cosmetic composition containing an epoxidized oil as plasticizer
6. Recent Progress in Synthesis of Glycerol Carbonate and Evaluation of Its Plasticizing Properties
7. YIKES: Acrylates Copolymer in Beauty Products
8. Water-based nail-polish composition
9. Polymer for water-based nail polish SYNTRAN® PC 5620
10. My List of Water Based, Peelable & Odourless Non-Toxic Nail Polish
11. Working the Nail Polish, Acquarella
12. Green Science Alliance Has Developed Water Base 100% Nature Biomass Nail Polish, Nail Color Which Does Not Come Off Even After Washing
13. Business Case for Acquarella.
14.
15.