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Stabilizer Technologies and their functionality in Candle Formulations

The 5th WORLD CANDLE CONGRESS
April 7th, 2016

Topics

- Evolution of stabilizers in candles
- The need for stabilizers in candles
- Thermal and UV stabilizer overview
  - Chemistries of each of the base classes
    - Phenolic Antioxidants
    - Secondary Antioxidants (peroxide decomposers)
    - Hindered Amine Light Stabilizers (HALS)
    - Ultraviolet (UV) Absorbers
- Formulation variables and synergies
- Summary

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Evolution of Stabilizers for Candles

- Butylated Hydroxytoluene (BHT) is a common antioxidant used to stabilize wax
  - Typically added at 50 to 100 ppm level by wax manufacturers
  - BHT causes color changes by a reaction which creates an unstable color species
  - Discoloration can occur in packaging prior to light exposure
  - Can be antagonistic with Hindered Amine Light Stabilizers (HALS)

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Evolution of Stabilizers for Candles

- Benzophenone and benzotriazole UV absorbers were introduced to the candle industry in late 1980s and early 1990's to protect formulations with complex fragrance chemistry and dyes that are not light stable
- The primary UV absorbers used in candle formulations are UV-5411, UV-328 and UV-531
- In the late 1990's and early 2000's, Hindered Amine Light Stabilizers (HALS) radical scavengers were introduced to the candle industry
- Red shifted benzotriazole UV absorbers with high molar efficiency were pursued but did not gain traction

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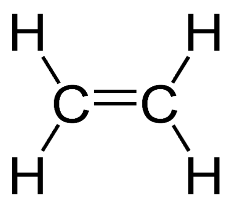
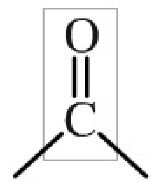
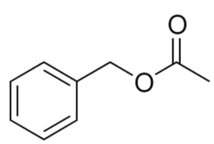
Unstable (LIGHT / HEAT) Chemical Bonds

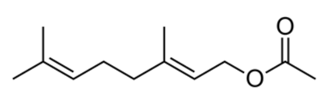
- Unsaturation and unhindered carbonyl bonds

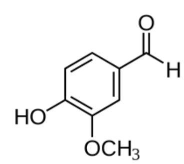


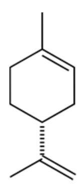


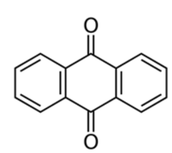
- Conjugated chemical bonds allow for color but are more susceptible to thermal and photo oxidation
- Examples of fragrance and dye chemistry - the nature of the chemistry makes them thermally and chemically very sensitive to degradation
  - Esters
  - Terpene
  - Aldehydes
  - Azo Compounds
  - Triaryl methane

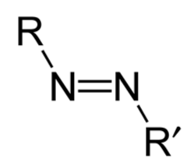


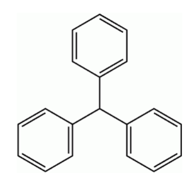




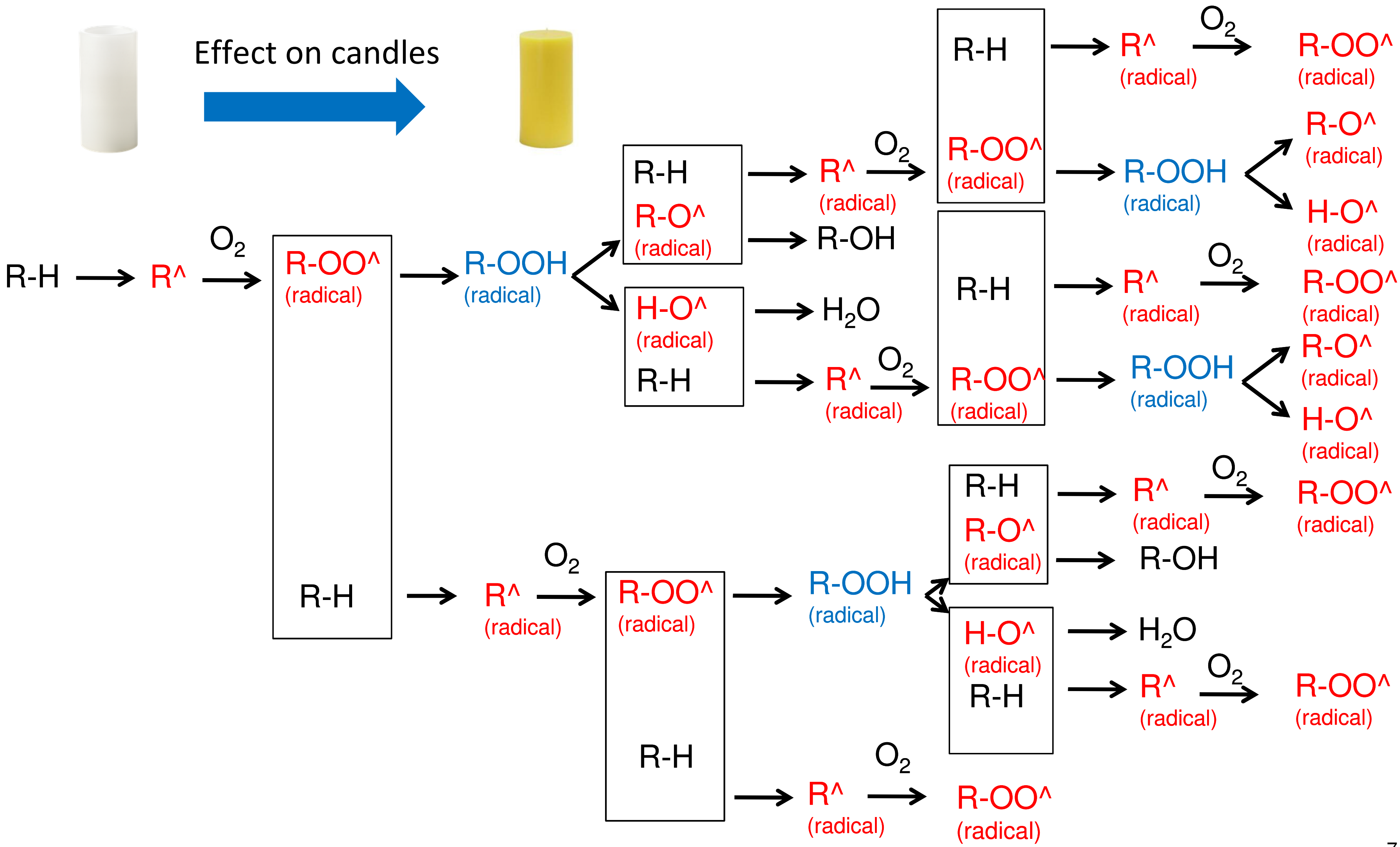








The Oxidation Cascade



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Stabilizer Functionality

- Trapping chemical intermediates in the oxidation process
  - Free radicals and hydro-peroxides
- Screening harmful ultraviolet radiation
- Different kinds of stabilizers are needed to prevent thermal as opposed to photo-oxidative degradation
  - Antioxidants and processing stabilizers
  - Light stabilizers

Stabilizer Functionality

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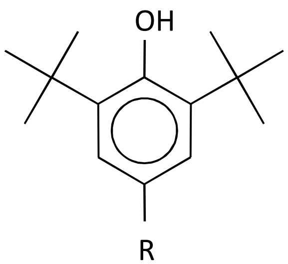
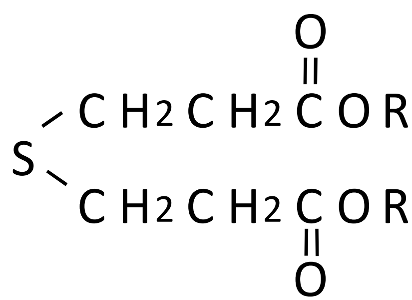
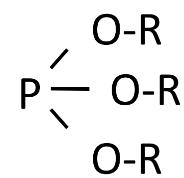
	Processing (180° C)	Long Term Heat Aging (100-160°)	Light Stability
HALS	No	Yes (125° C)	Yes
Phenolic	Yes	Yes	No
Phosphite	Yes	No	No
Thio-synergist	Yes	Yes (150° C)	No
UV Absorber	No	No	Yes



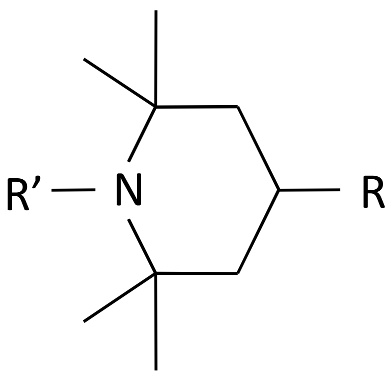
Phenolic (Primary Antioxidant)



Thio-synergist (Secondary Antioxidant)

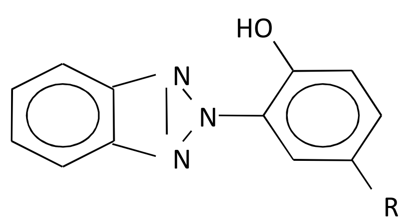


Phosphite (Secondary antioxidant)

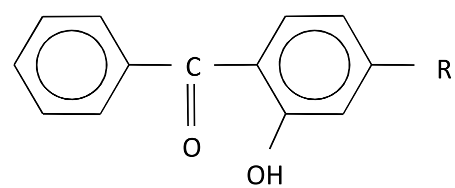


HALS- Hindered Amine Light Stabilizer

(Primary AO- Radical Trap)



UV Absorber - Benzotriazole



UV Absorber--Benzophenone

Stabilizer Functionality

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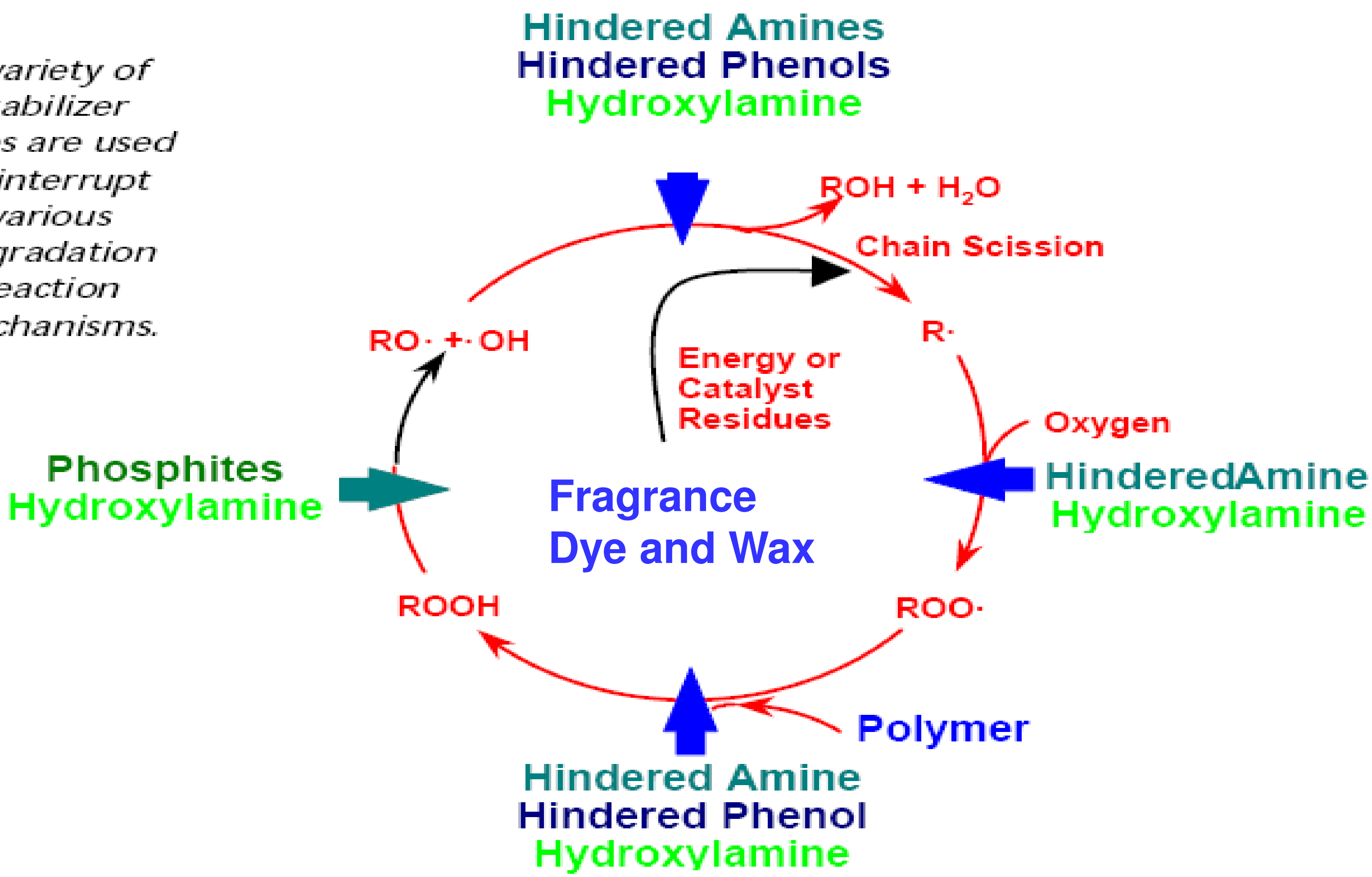
A variety of stabilizer types are used to interrupt various degradation reaction mechanisms.



Topics

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- The need for stabilizers in Candles
- Thermal and UV stabilizer overview
    - Chemistries of each of the base classes
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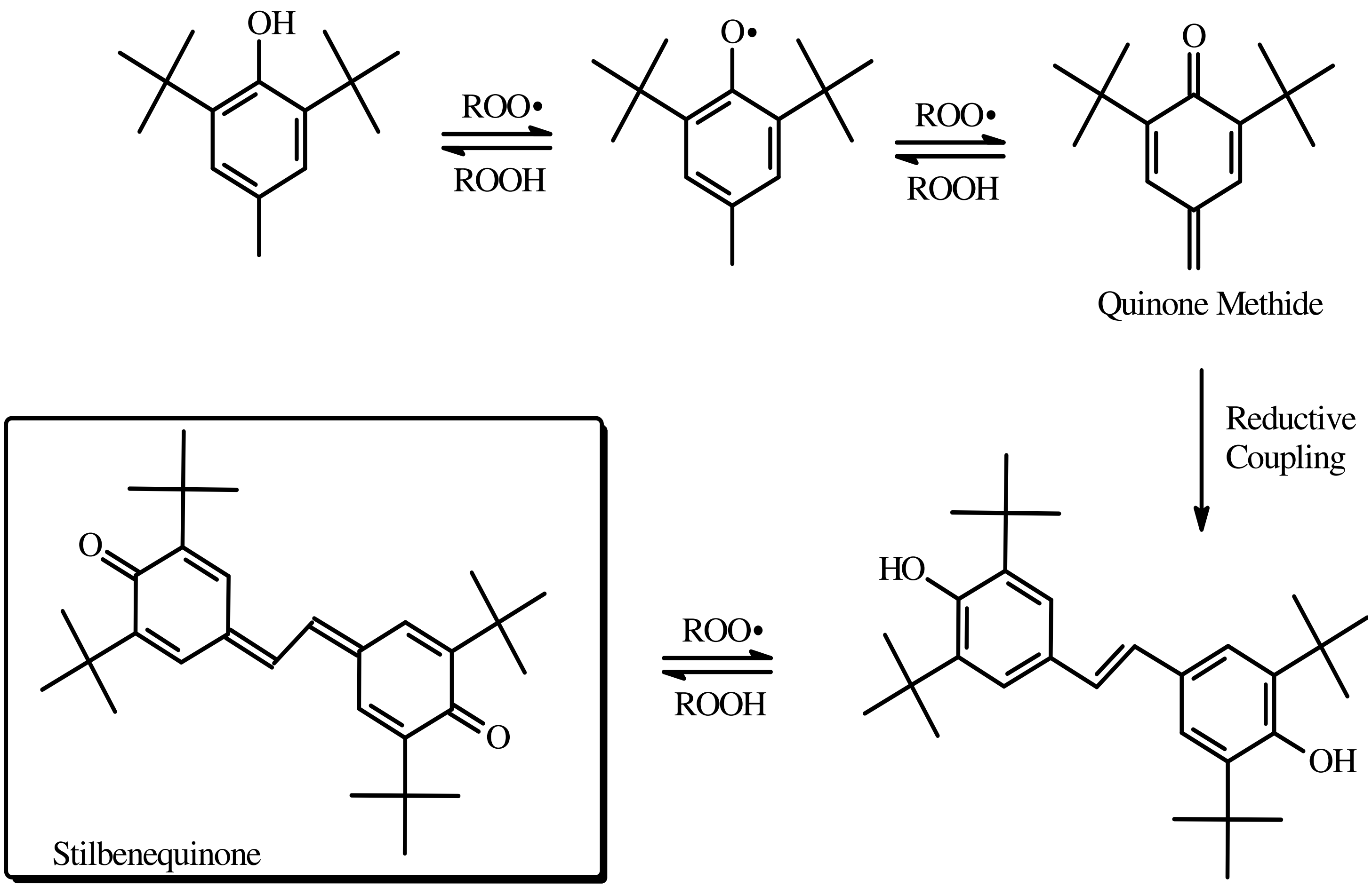
        - Ultraviolet (UV) Absorbers
    - Synergistic and antagonistic effects
    - Summary

Hindered Phenols

- The largest group of antioxidants
- Provide protection during processing and long term heat exposure in the liquid and solid phase
- Function mainly by scavenging peroxy radicals (primary antioxidants)
- Oxidation products of hindered phenols can be discoloring

Phenolic Mechanism - Color Body Formation



Phosphites

- Phosphites are highly effective processing stabilizers, especially when used in combination with hindered phenols
- Function by decomposition of hydroperoxides (secondary antioxidants)
- Phosphites are subject to hydrolysis
  - Phosphite 168 exhibits better hydrolytic stability as compared to most other phosphites
  - Balance between performance and moisture sensitivity

Light Stabilizers

- Objective:
  - Extend the lifetime of candles and other materials that are exposed to UV or fluorescent light in storage, on display

    and in use
- Two main families of light stabilizers
  - UV absorbers
  - Hindered Amine Light Stabilizers (HALS)

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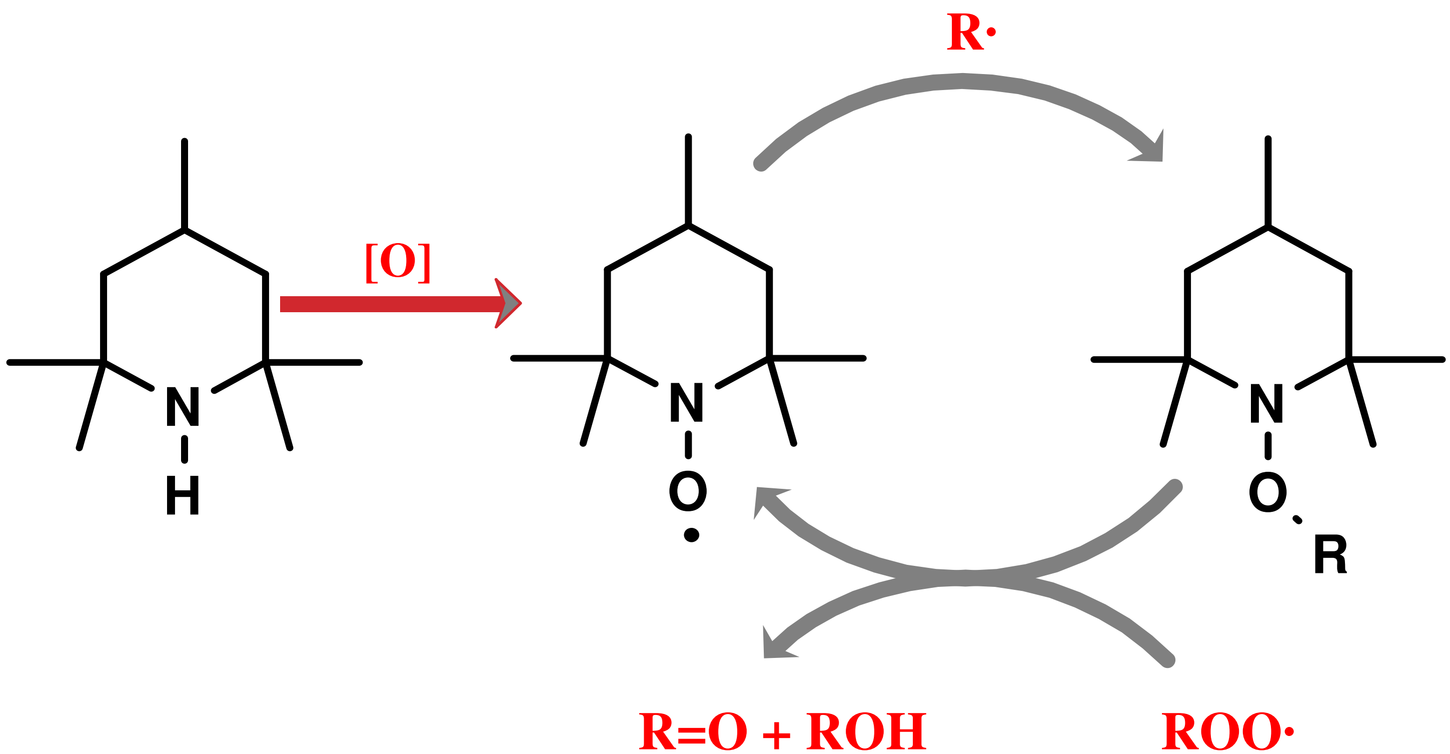
HALS (Hindered Amine Light Stabilizers)



- Regenerative radical scavenging mechanism

Note: Denisov cycle is an oversimplification of the reaction that takes place

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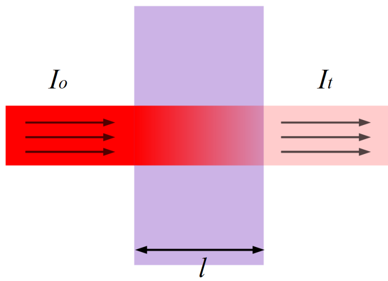
UV Absorbers

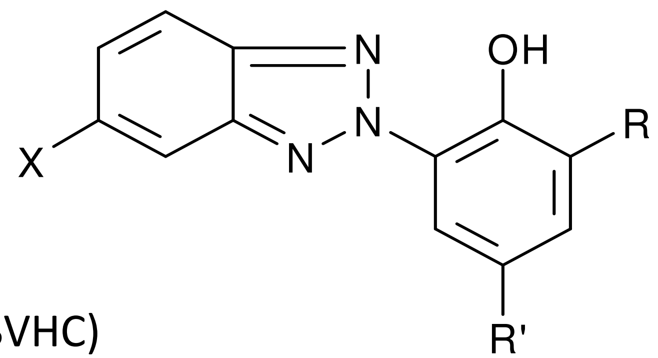
- UV absorbers limit the penetration depth of damaging UV and fluorescent light into the candle
  - Below this critical depth, no degradation takes place
  - Above this depth, degradation is slowed but not stopped
- This effect can improve retention of physical properties and or reduce discoloration associated with light exposure



A = e (molar absorptivity) * l (path length) * c (concentration)

Benzotriazole UV Absorbers

- Widely used UV absorbers for candles and other materials
- Broad spectral coverage in UV-A and UV-B region
- Low color contribution due to minimal absorbance in the visible region (>400 nm)
- Products with wide range of secondary properties (*e.g.* volatility, melting point) are available
- Can be interactive with metals and form color bodies
- UV 328 identified as a Substance of Very High Concern (SVHC)



	X	R	R’
UV 1710	H	H	CH_3
UV 5411	H	H	$t\text{-}C_8H_{17}$
UV 328	H	$t\text{-}C_5H_{11}$	$t\text{-}C_5H_{11}$
UV 326	Cl	$t\text{-}C_4H_9$	CH_3
UV 234	H	*t*-cumyl	*t*-cumyl

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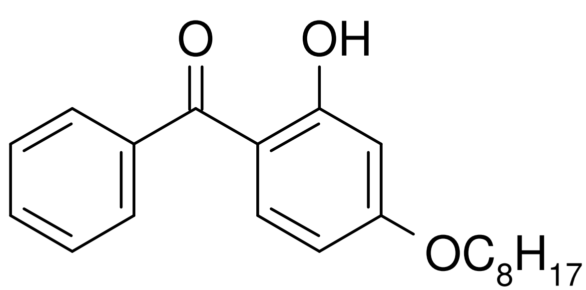
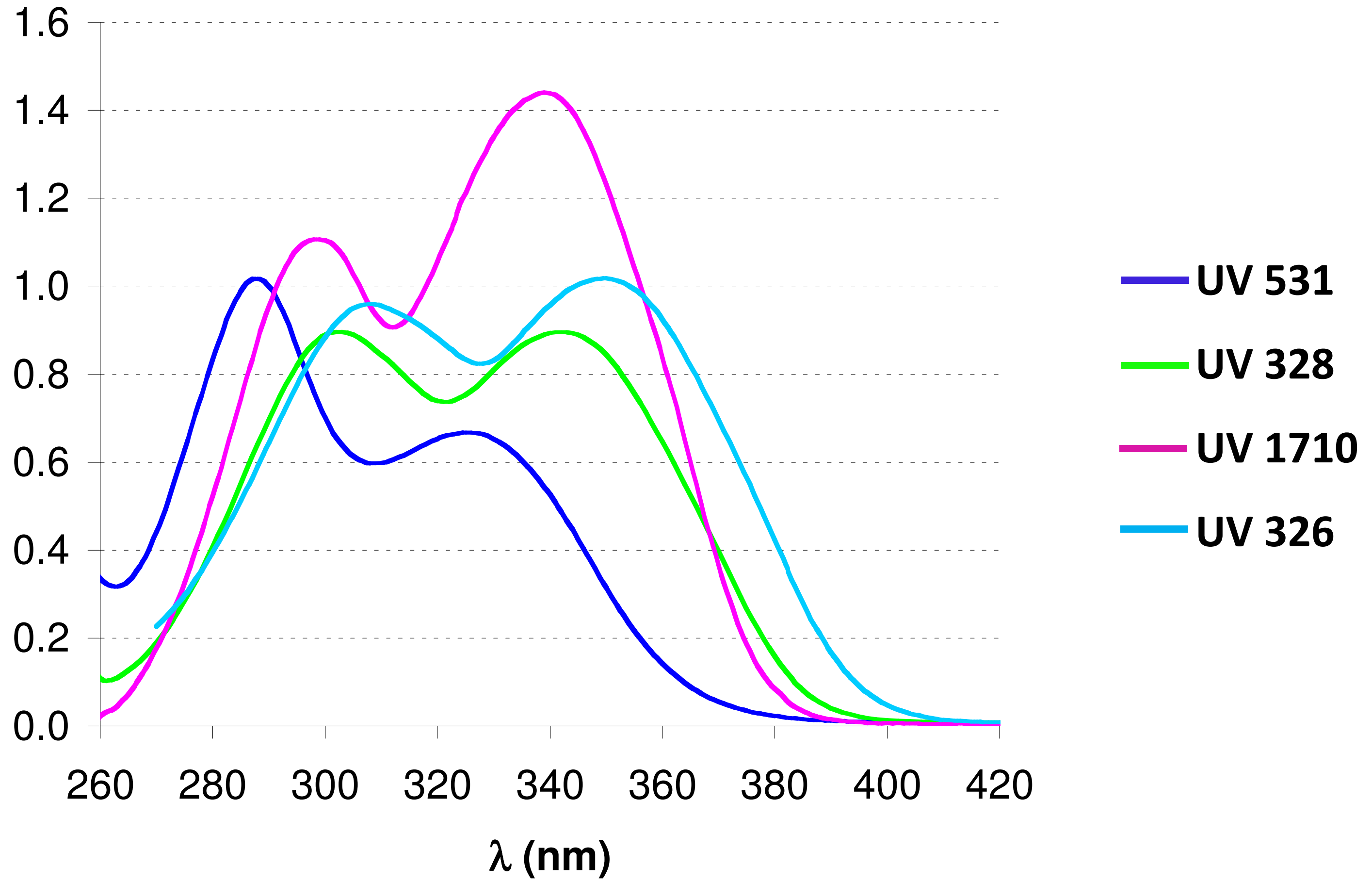
Benzophenone UV Absorbers

- Widely used UV absorbers for candles and other materials
- Different UV absorption characteristics compared to benzotriazole UV absorbers
  - Stronger absorbance in UV-B region, weaker in UV-A region
- Compatible with paraffin waxes and substrates (greater than benzotriazole UV absorbers)

UV 531



UV Absorbance Spectra



20 mg/L in ethyl acetate

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- **Synergistic and antagonistic effects**
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Formulation Variables and Synergies

Materials used in candle formulations

- Variety of waxes used in candle formulations
  - Provides a range of properties and functional attributes
- Complex fragrance compounds and chemistries
- Ever changing color demand and unstable dyes
- Polymeric additives (hyper-branched polymers)
- Other materials and considerations

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Formulation Variables and Synergies

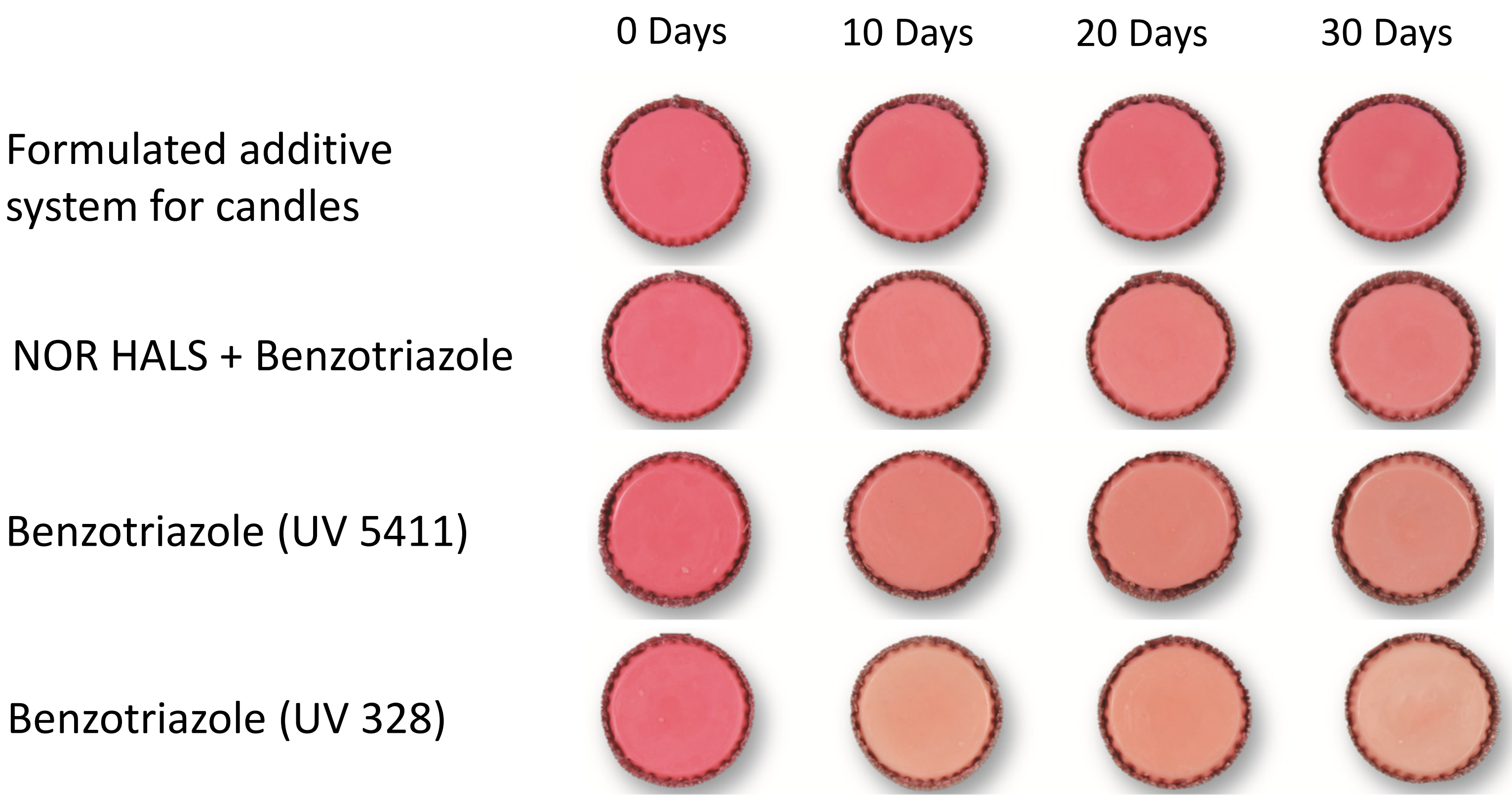
Significant selection of additives for stabilization

- Continuously changing chemical regulatory landscape
- Consolidation in the additive and chemical industry
  - Product discontinuation and supply constraints

Understanding and knowing the chemistry is critical to selection of the appropriate stabilizer package

- Stabilizer synergies can deliver significant performance improvements
- Consideration to burn properties of candle
- Potential impact to fragrance characteristics

Examples of Synergistic Effects



- Formulation: 70/30 Paraffin/Soy wax blend, 4% vanilla fragrance, 0.04% dye, 0.2% UV additive
- Exposure to fluorescent lights 12” from source

Examples of Synergistic effects

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0 Days | 10 Days | 20 Days | 30 Days

Formulated additive system for candles

NOR HALS + Benzotriazole

Benzotriazole (UV 5411)

Benzotriazole (UV 328)

- Formulation: 70/30 Paraffin/Soy wax blend, 4% vanilla fragrance, 0.04% dye, 0.2% UV additive
- Exposure to fluorescent lights 12” from source

Summary

- When selecting additives synergistic and antagonistic effects are possible
- Hundreds of stabilizer products and thousands of stabilizer combinations
- Additive expertise and knowledge is critical to selecting stabilizers that provide the highest performance and value
- Additive system formulations provide more value and improved performance

Questions and Answer Time

Contact Information:

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