

# On the Mitigation of Threats to “Business as Usual” in the Additives Realm

Rob Lorenzini, Ph.D. – Maroon Group LLC



Additives



Pigments



Creative  
Functional  
Polymers



Custom  
Blends &  
Repackaging

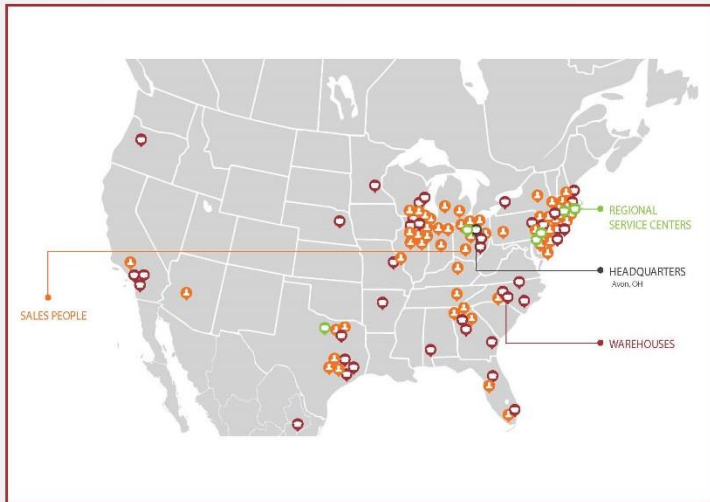


**Consistent Products ... Consistent Delivery ... Consistent Supply**



## Specialty Chemical Distributor & Formulary Partner

Maroon Group supplies specialty additives, resins, pigments, intermediates, and ingredients to customers across North America.



## KEY MARKETS

- Thermoplastics
- CASE
- Personal Care
- Food
- Pharmaceutical
- Electronics
- HI & I

## KEY STATISTICS

- Founded: 1977
- Employees: ~225
- Account Managers: 73
- Service Centers: 7
- Active Customers: 4,600+
- Warehouses: 40
- Import Countries: 20



# | Agenda

## **Tariffs**

- General commentary

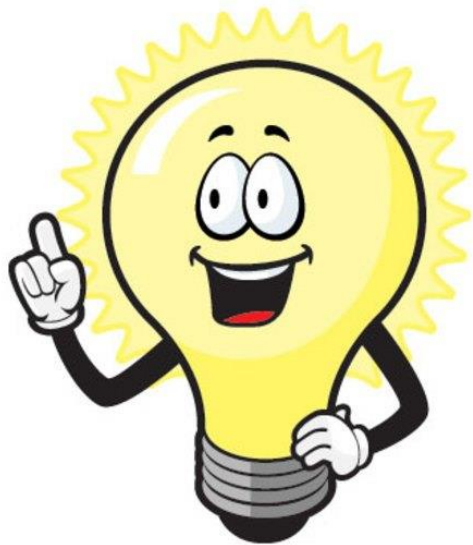
## **Shortages of Raw Materials**

- China's Blue Sky Initiative
- 2018 HALS shortage – hexamethylenediamine
- Ongoing resorcinol price increases

## **Regulatory Challenges**

- What's going on with UV absorbers?
- What about trace materials? 2,4-di-*t*-butylphenol

# Formulary Prowess and Strong Regulatory Understanding Can Mitigate Your Risk



# Some Quick Notes

**I'm not here to sell you any products. Seriously.**

These slides don't use tradenames, and rely on structure-property relationships, “tribal knowledge”, spectral data, and the primary literature. Sit back and enjoy the education!

**I am here to sell you an idea – in these times, we need to kill the Appeal to Tradition!**

Appeal to tradition (also known as *argumentum ad antiquitatem*, appeal to antiquity, or appeal to common practice) is an argument in which a thesis is deemed correct on the basis that it is correlated with some past or present tradition. The appeal takes the form of “**this is right because we've always done it this way.**” \*\*

**I will speak with the best-known numbering schemes generically, e.g. AO-168**

Lots of names out there for the same material, but this makes communication easier

**X is not a drop-in for Y!**

Change is good, **but change requires work**

These slides hypothesize reformulations based on an urgent need in response to a supply or regulatory threat – **always quantifiably verify for your application!**

\*\* Trufant, William (1917). *Argumentation and Debating*.

# | Tariffs

To avoid political commentary, some (hopefully) objective, brief statements:

Many stabilizers and other raw materials/intermediates are produced in China

We exist in a global economy – does everybody actually make everything?

If a chemistry were to evaporate overnight, would you have a backup formulation?

Don't get surprised, don't get shut down – weathering takes a long time

- Start **NOW!**
- Invest the time in a proper FMEA
  - The first real disruption for the “freshman and sophomore class” in the industry
  - Veterans: \*yawn\*

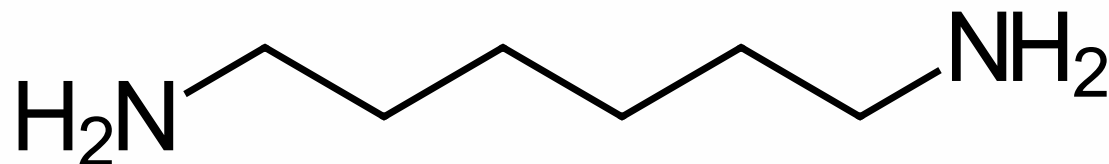
# | Shortages of Raw Materials

**China's Blue Sky Initiative** is showing no signs of relenting, as manufacturing sites continue to be shut down – temporarily for inspections, and permanently for non-comformance

**The potential for abrupt shortages is still on the table**

Manufacturers **continue their efforts in compliance** and continue to **move to “industrial parks”**

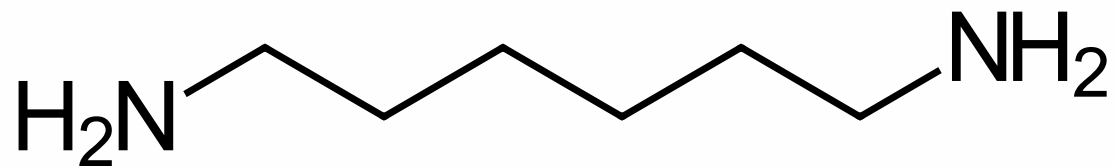
# | Shortages of Raw Materials – HALS



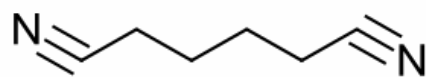
Hexamethylenediamine



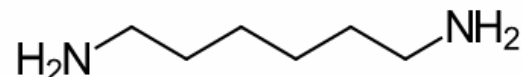
# Shortages of Raw Materials – HALS



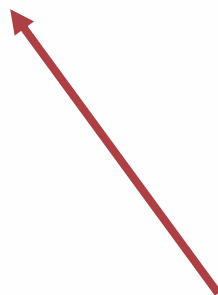
Hexamethylenediamine



Adiponitrile

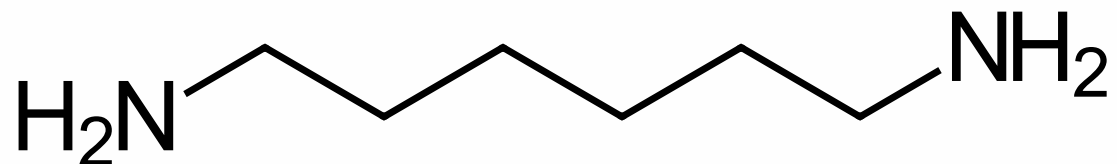


Hexamethylenediamine  
(HMD)



Force majeure, global supply issues

# | Shortages of Raw Materials – HALS

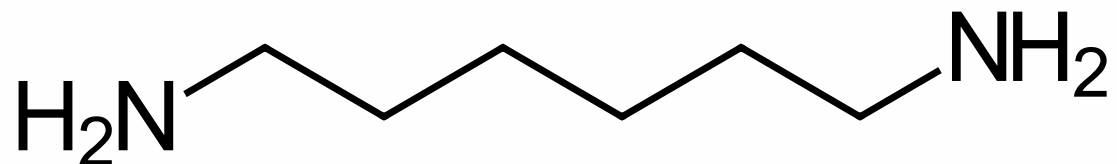


Hexamethylenediamine



**Skeptical Purchasing Professional  
Irritated Technical Professional**

# | Shortages of Raw Materials – HALS

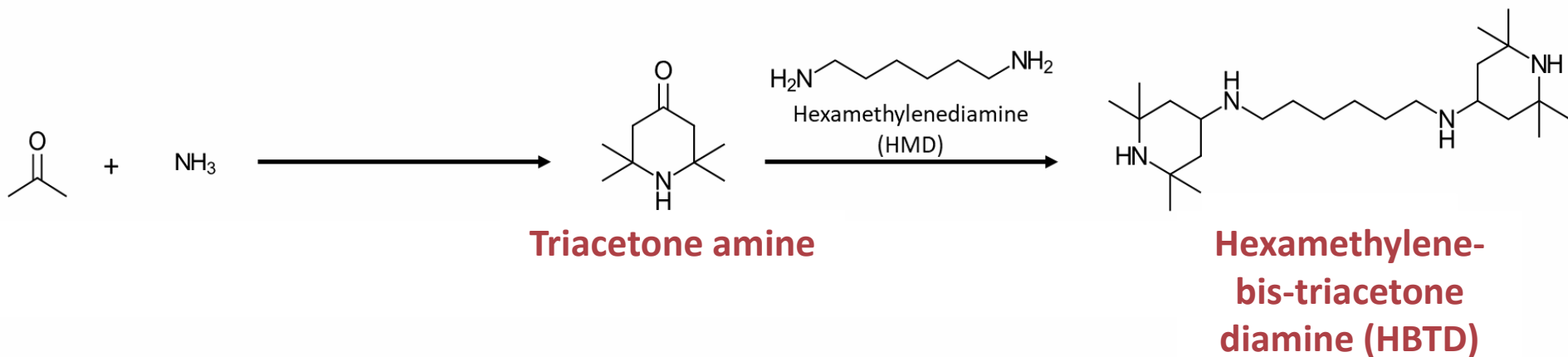


Hexamethylenediamine

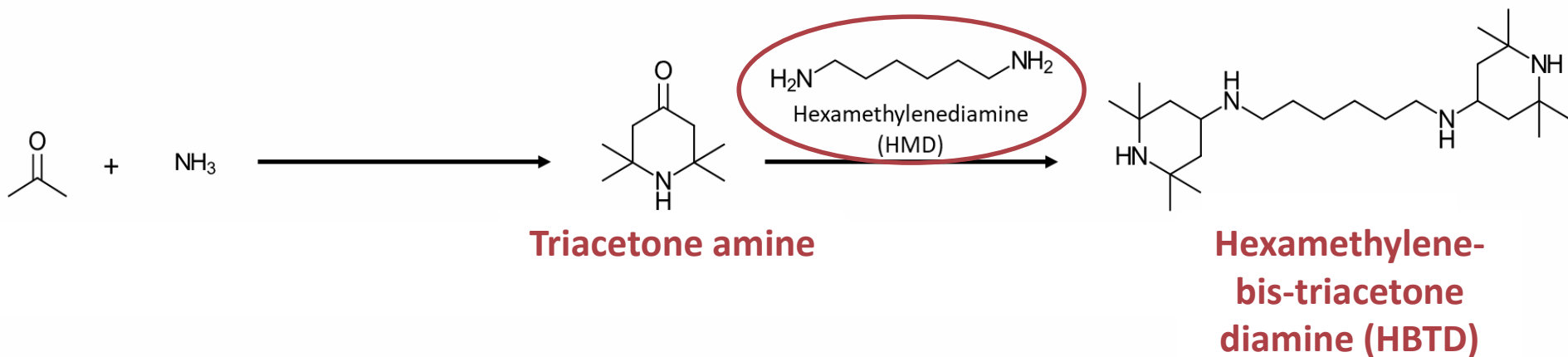
Great story. Who cares?  
I get it for Nylon folks, but  
I work with polyolefins.



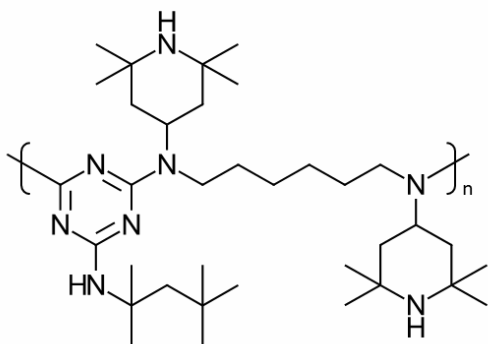
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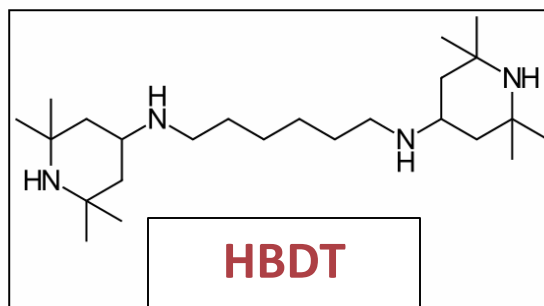
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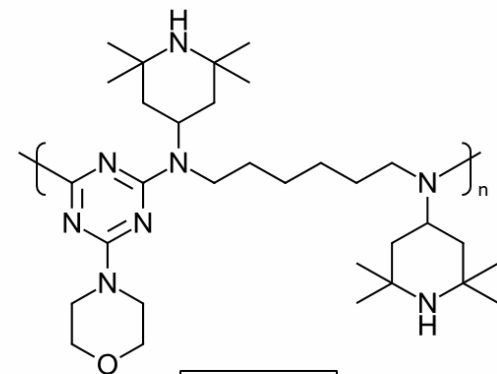
# Shortages of Raw Materials – HALS



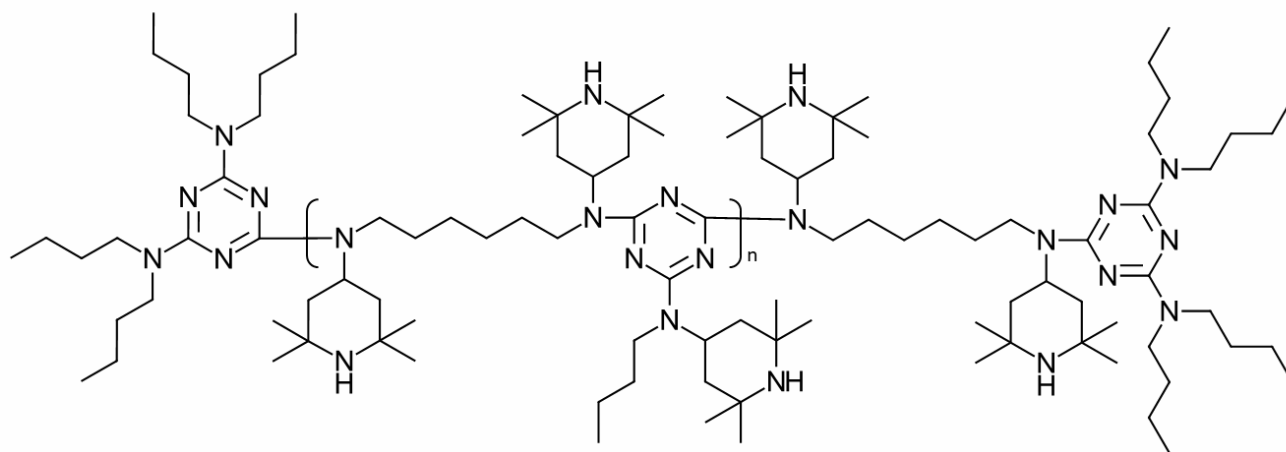
HALS 944



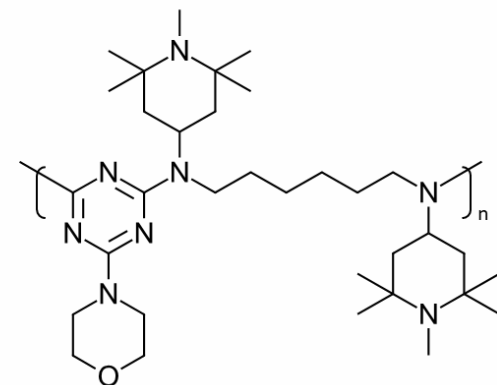
HBDT



HALS 3346



HALS 2020



HALS 3529

# | Shortages of Raw Materials – HALS

Can you reformulate out of a bad situation?  
Are your suppliers playing an honest game?

## Common HALS made with HBDT\*

UV-944 – High MW N-H HALS  
UV-3346 – High MW N-H HALS  
UV-2020 – High MW N-H HALS  
UV-3529 – High MW N-CH<sub>3</sub> HALS

## Common HALS made without HBDT

UV-770 – Low MW N-H HALS  
UV-765 – Low MW N-CH<sub>3</sub> HALS  
UV-3853 – Low MW N-H HALS  
UV-119 – High MW N-CH<sub>3</sub> HALS  
UV-622 – “it’s complicated”  
UV-4050 – Low MW N-H HALS  
UV-5050 – High MW N-H HALS

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UV-5050 – High MW N-H HALS

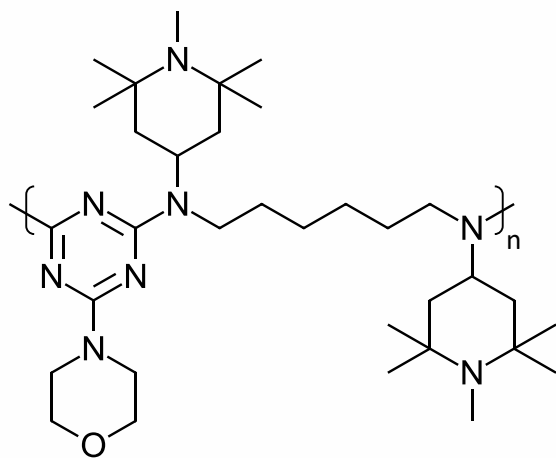


# Shortages of Raw Materials – HALS

An example – the “easier” one

UV-3529 → UV-119

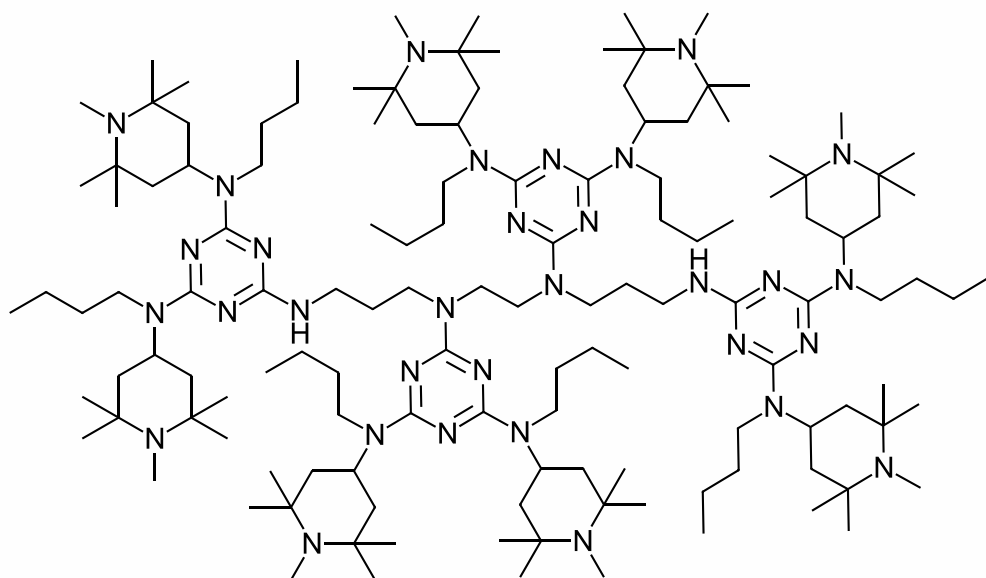
High molecular weight N-CH<sub>3</sub> HALS



**UV-3529**

MW = ~1700 g/mol\*\*

MP = 85-95°C



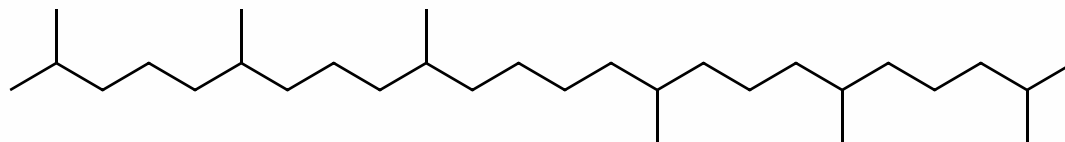
**UV-119**

MW = 2286 g/mol

MP = 115-150°C

## Shortages of Raw Materials – HALS

## HALS stabilizer efficiency in squalane (PP mimicking solvent)



## 0.25% HALS

After 176 and 541 h samples were withdrawn, squalane degradation products were extracted as described in Section 2.3 and quantified with HPLC-QQQ-MS. As reported recently, **comparison of the peak areas of the four most abundant carbonylic squalane oxidation products allowed performing a “stabilizer efficacy rating”**

Stabilizer Combo	176h Xenon Aging	541h Xenon Aging
UV-3529 + AO-1330	79%	61%
UV-119 + AO-1330	91%	77%

Maringer, L., Roiser, L., Wallner, G., Nitsche, D., Buchberger, W. *Polym Degrad Stab* 131 (2016) 91-97

# Shortages of Raw Materials – HALS

Inhibition rate constants – a measure of HALS activity

“Rate constants for the addition of cumylalkyl radicals to the...reference alkyl radical scavenging stabilizers”

Stabilizer	Rate Constant, $k_{(333K)} \text{ M}^{-1}\text{s}^{-1}$
UV-3529	$(2.0 \pm 0.8) \times 10^8$
UV-119	$(1.4 \pm 0.2) \times 10^8$

Magerramova, M.Y., Salmanova, N.I., Zeynalov, E.B. *IJSET* (2015), 2, 11, 885-897

# | Shortages of Raw Materials – HALS

Can you reformulate out of a bad situation?  
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UV-944 – High MW N-H HALS

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UV-622 – “it’s complicated”

UV-4050 – Low MW N-H HALS

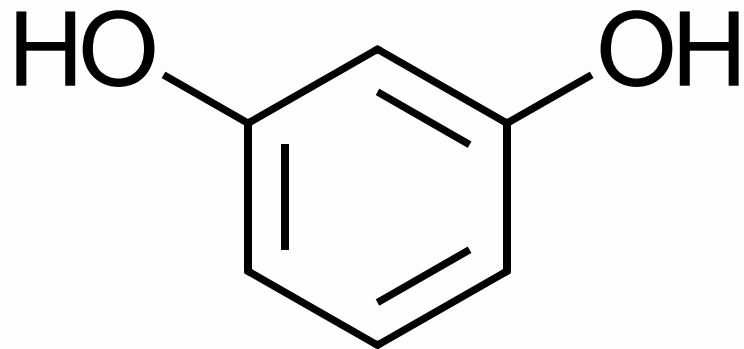
UV-5050 – High MW N-H HALS

# | Shortages of Raw Materials – HALS

**“It depends!”**

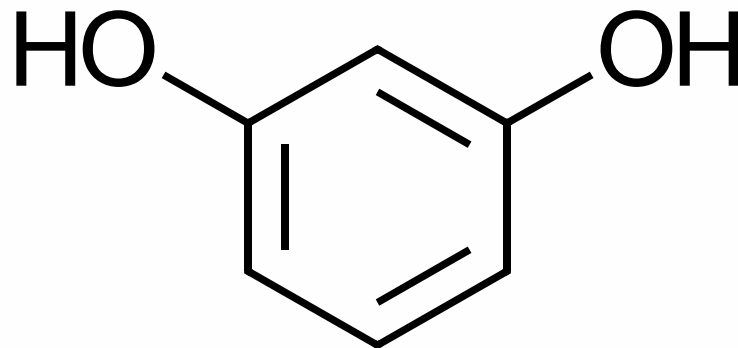
- Thickness of polymer article – high vs. low MW HALS
- Surface vs. bulk protection – high vs. low MW HALS
- Chemical resistance/less prone to side reaction – N-H vs. N-CH<sub>3</sub>
- Service life requirements – Heat? Light? Both?
- Always test your replacement formulations!

# | Shortages of Raw Materials – Resorcinol



Resorcinol  
Benzene-1,3-diol

# | Shortages of Raw Materials – Resorcinol

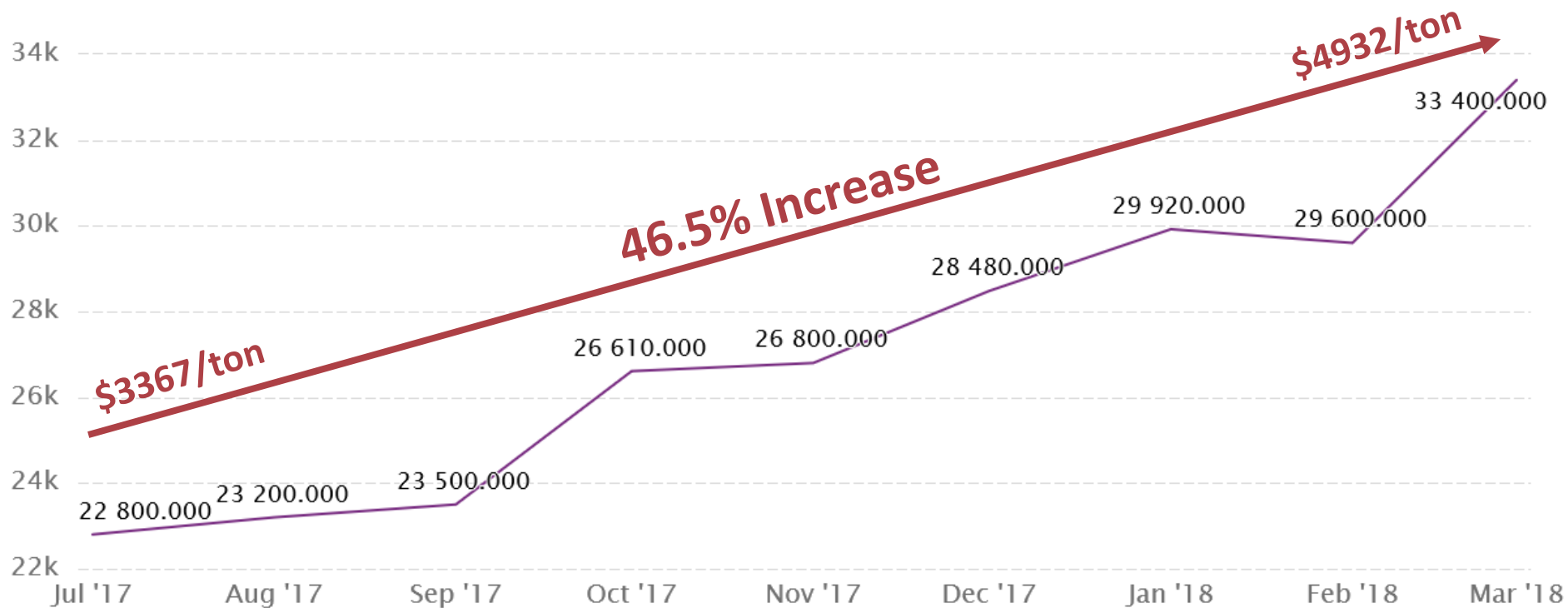


Resorcinol  
Benzene-1,3-diol



# Shortages of Raw Materials – Resorcinol

China CN: Market Price: Monthly Avg: Organic Chemical Material: Resorcinol 99.9%

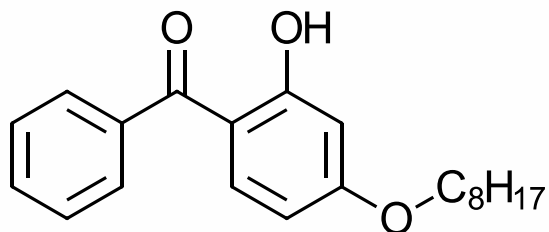


■ CN: Market Price: Monthly Avg: Organic Chemical Material: Resorcinol 99.9%

SOURCE: WWW.CEICDATA.COM | China Petroleum and Chemical Industry Federation



# Shortages of Raw Materials – Resorcinol

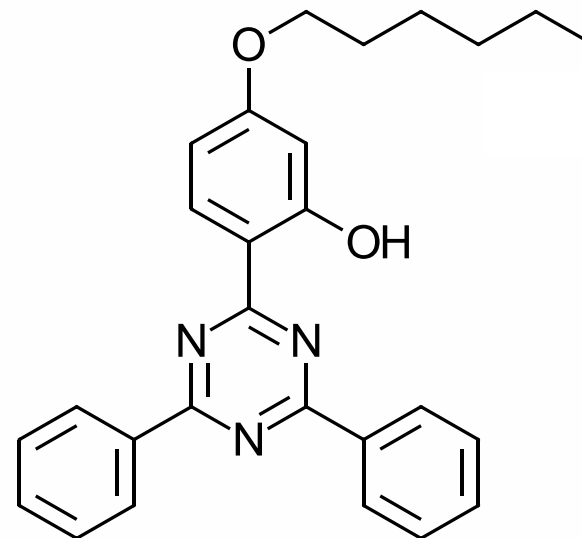


## Benzophenones

UV-9 / BP-1

UV-24 / BP-8

UV-531 / UV-81 / BP-12



## Triazines

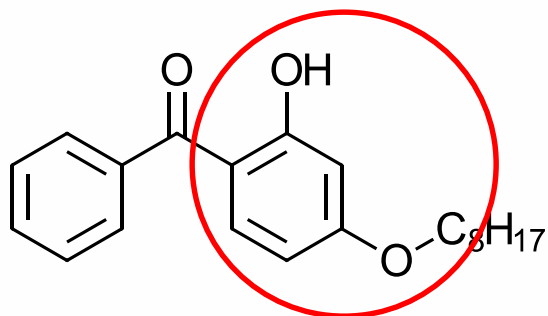
UV-1577

UV-1164

UV-400

UV-405

# Shortages of Raw Materials – Resorcinol

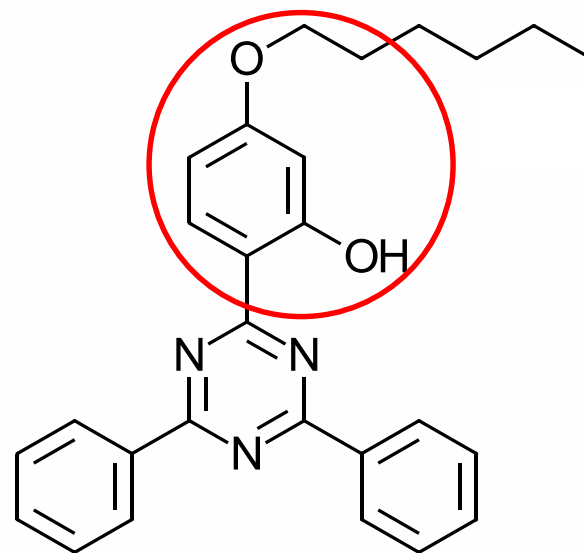


## Benzophenones

UV-9 / BP-1

UV-24 / BP-8

UV-531 / UV-81 / BP-12



## Triazines

UV-1577

UV-1164

UV-400

UV-405

# | Shortages of Raw Materials – Resorcinol

## Beer's Law

$$A = c\epsilon l$$

$A$  = Absorbance

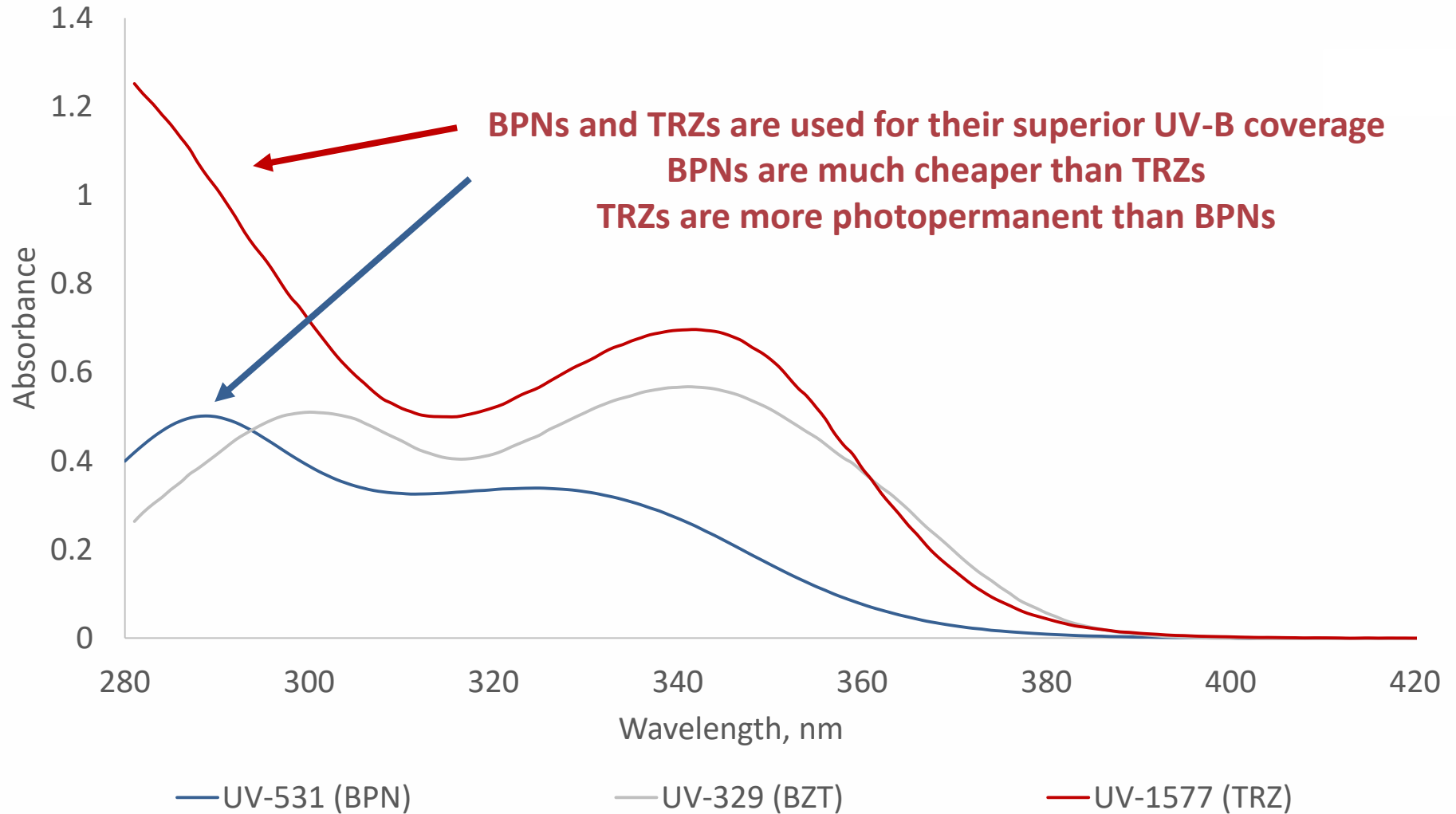
$c$  = Concentration

$\epsilon$  = Absorption Coefficient

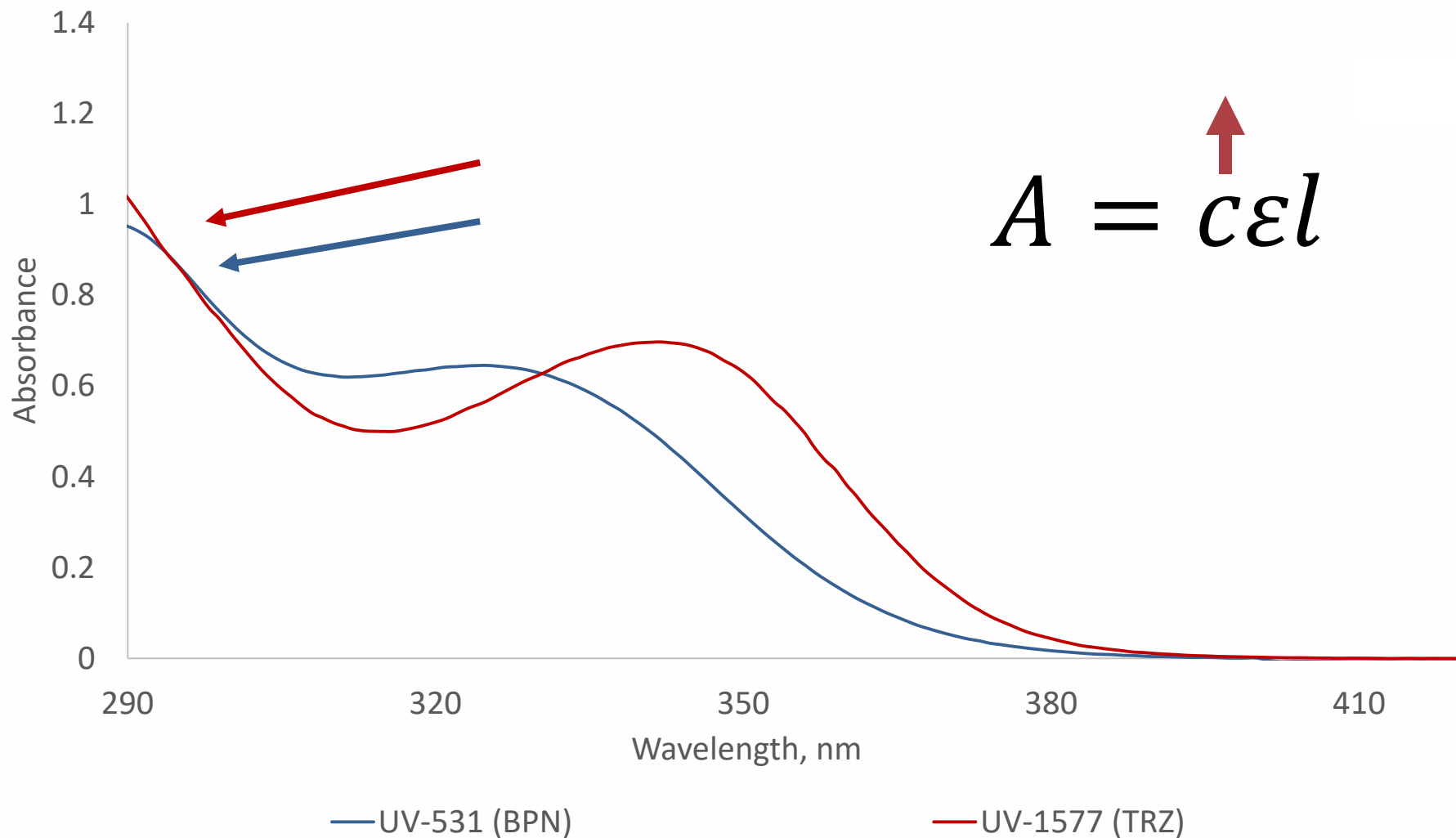
$l$  = Pathlength

**Calculations based on solution state – same principals in polymer**  
**Need to account for inherent polymer absorption**

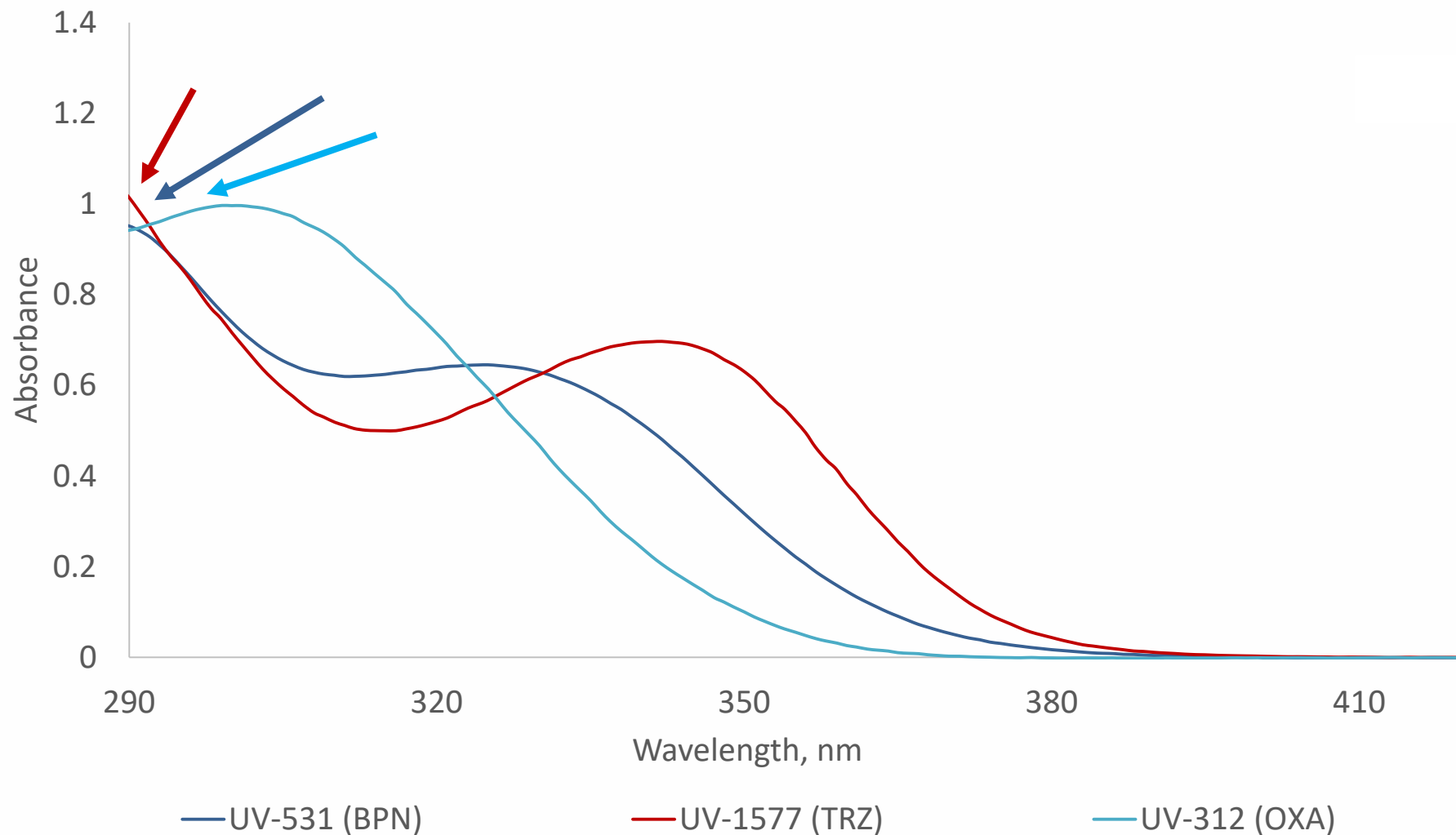
# Shortages of Raw Materials – Resorcinol



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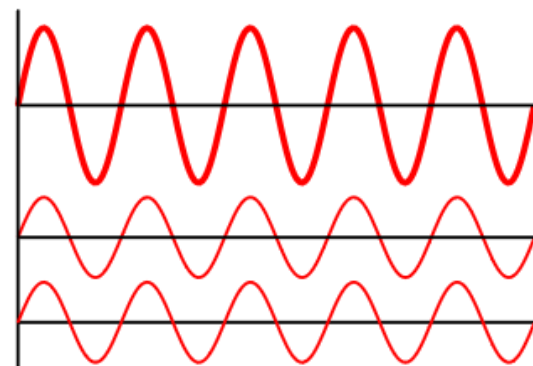
Just an example – feel empowered! Get creative!

## “Off-label” uses for stabilizing chemistries

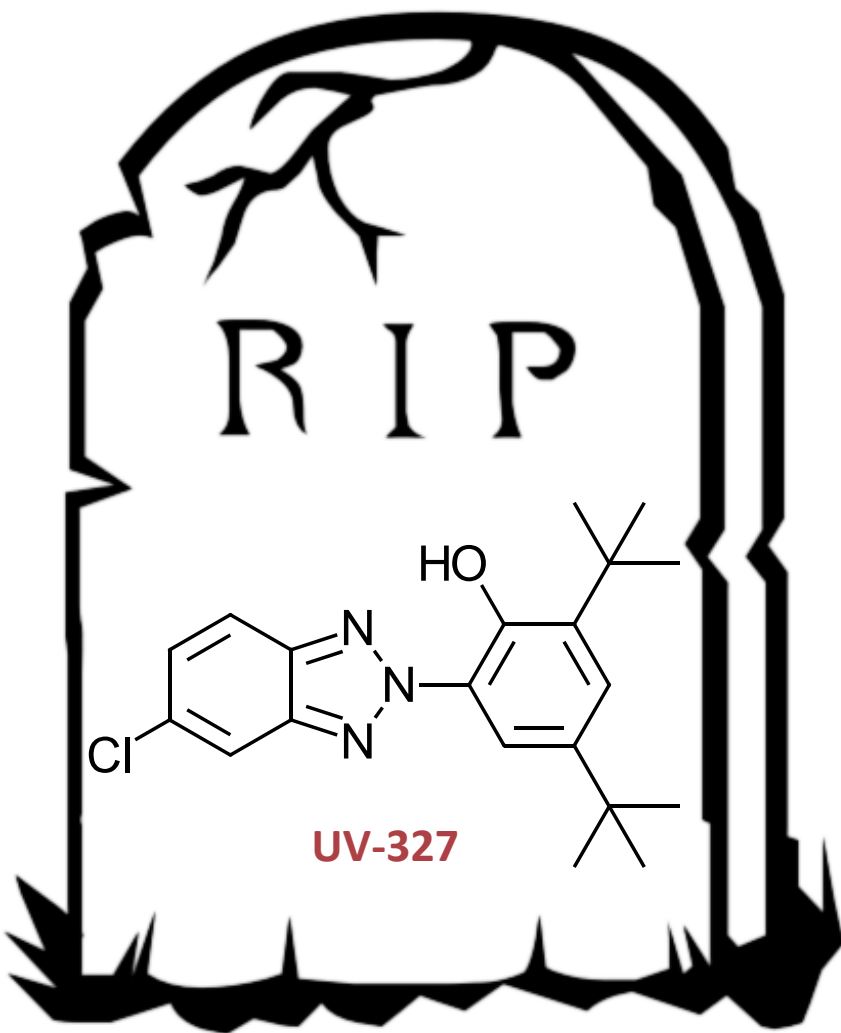
- Borrow additives from other polymers and markets
- Due diligence – exudation/blooming, processing, etc.

## UV absorbers behave with “Constructive Interference”

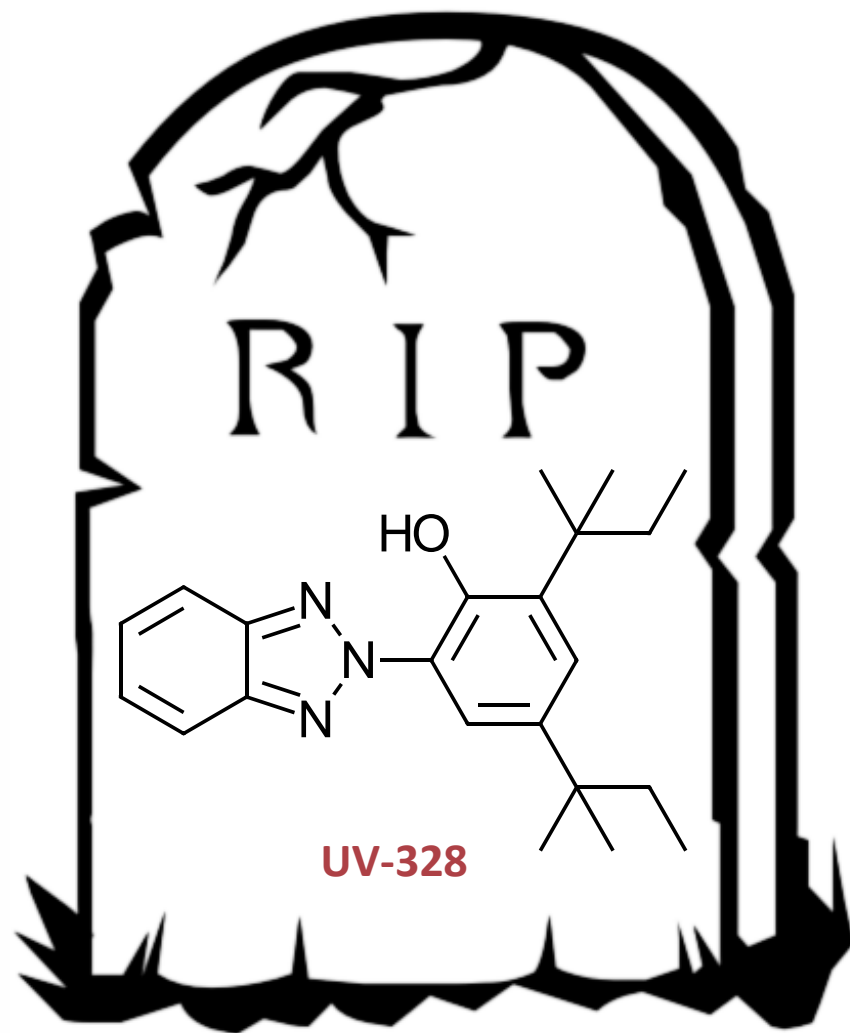
- Different classes of absorbers
- Different loadings
- **Warning!** When blending, check the patent art
  - “Blends Wars” strong about ~20 years ago – re-read the art!



# Regulatory Challenges



?





# | Regulatory Challenges

## Which Seven Substances Have Been Recommended For Authorisation?

ECHA's eighth recommendation to the European Commission to prioritise SVHCs for inclusion in the Authorisation List contains the following seven substances:

- **5-sec-butyl-2-(2,4-dimethylcyclohex-3-en-1-yl)-5-methyl-1,3-dioxane [1], 5-sec-butyl-2-(4,6-dimethylcyclohex-3-en-1-yl)-5-methyl-1,3-dioxane [2] [covering any of the individual stereoisomers of [1] and [2] or any combination thereof] (*karanal group*):** Used as a fragrance in soaps and detergents, this substance has been recommended for its vPvB properties.
- **2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol (*UV-328*):** Used as a UV stabiliser; for example in plastic products, rubber and coatings, this substance has been prioritised for its PBT and vPvB properties.
- **2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol (*UV-327*):** Although this substance has no registered uses, it has been recommended for authorisation based on its structural similarities with (*UV-328*).
- **2-(2H-benzotriazol-2-yl)-4-(tert-butyl)-6-(sec-butyl)phenol (*UV-350*):** Although this substance has no registered uses, it has also been prioritised based on its structural similarities with (*UV-328*).
- **2-benzotriazol-2-yl-4,6-di-tert-butylphenol (*UV-320*):** Although this substance has no registered uses, it too has been recommended for authorisation based on its structural similarities with (*UV-328*).
- **1,2-benzenedicarboxylic acid, di-C6-10-alkyl esters; and 1,2-benzenedicarboxylic acid, mixed decyl and hexyl and octyl diesters with  $\geq 0.3\%$  of dihexyl phthalate (*EC 201-559-5*):** Used as a plasticiser in PVC compounds and as an adhesive, these substances have been recommended for the Authorisation List as they are considered to be toxic for reproduction. (Whilst these are technically two substances, they have been grouped together as the second substance is not registered, and therefore no information is available).
- **1-methyl-2-pyrrolidone (*NMP*):** A widely used solvent in products such as coatings, cleaning agents and functional fluids, this substance has also been recommended for authorisation as it is considered to be toxic for reproduction.

<https://psi.ul.com/en/resources/article/echa-recommends-seven-new-substances-for-reach-authorisation-list/>

# | Regulatory Challenges

## **REACH – Annex XIV – “Authorization List”**

**Increasing regulatory burden in Europe – “does this impact me?”**

**Do business globally? Worth it to regionalize products? Risks?**

**Exit of major suppliers?**

**Leading edge of subsequent regulations -> California? FDA?**

# | Regulatory Challenges

**Other BZTs are being informally evaluated** under the PACT-RMOA program (UV-P, 234, 326, 329, 928)\*

Some analysis indicates **higher risk around UV-P and UV-234, and some risk around the others**, but nothing indicates that they meet the REACH criteria for PBT or vPvB based on available data\*

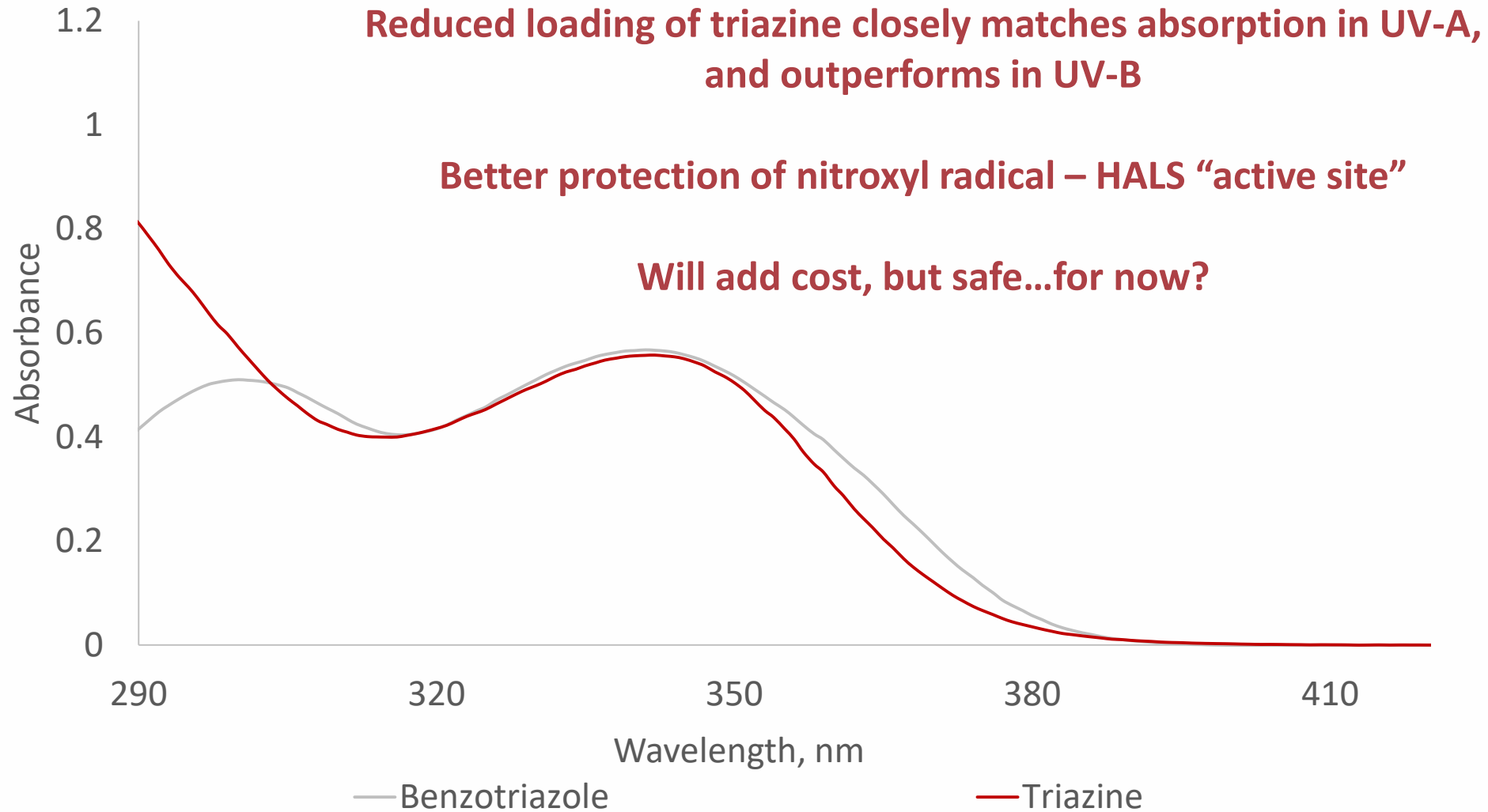
\* Botkin, J. *Substitution of Benzotriazole UV Absorbers in Plastics* – SPE Thermoplastic Elastomers TOPCON 2018

# | Regulatory Challenges

**A thought experiment:**

**What if the rest of the benzotriazoles abruptly disappeared?**

# Regulatory Challenges



# Regulatory Challenges

Triazines can be used at lower loadings, and will improve weatherability in many polymer systems, even after “matching” absorption spectra, because of their inherent photopermanence

Rate of loss of UVAs in PMMA films when exposed to xenon arc weathering. Rates as loss of absorbance per 1000kJ/m<sup>2</sup> @ 340nm xenon arc exposure

Stabilizer	Rate of Abs. Loss per 1000kJ/m <sup>2</sup>
UV-1164 (triazine)	0.085
UV-5411/UV-329 (benzotriazole)	0.11

Pickett, J.E. *Macromol. Symp.* 115 (1997) 127-141

Stabilizer	Rate of Abs. Loss per 1000kJ/m <sup>2</sup>
UV-1164 (triazine)	0.21
UV-5411/UV-329 (benzotriazole)	0.29

Pickett, J.E., Moore, J.E. *Polym Degrad Stab* 42 (1993) 231-244

# | Regulatory Challenges

Triazines show increased weathering performance in polyethylene and polypropylene at equal loadings – an argument to try at reduced loading for equal performance

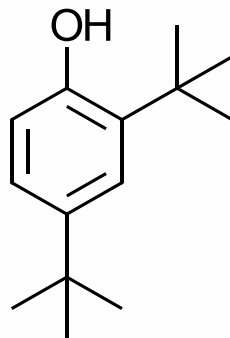
LLDPE Films  
8% nanoclay filler  
0.30% UV absorber  
0.2% MD-1024  
QUV-B Artificial weathering

Stabilizer	QUV-B Hours to 50% elongation @ break	QUV-B Hours to 50% tensile strength
Control	60	45
UV-1164 (triazine)	150	175
UV-328 (benzotriazole)	115	120

La Mantina, F.P. et al. *Polym Degrad Stab* 91 (2006) 3208-3213

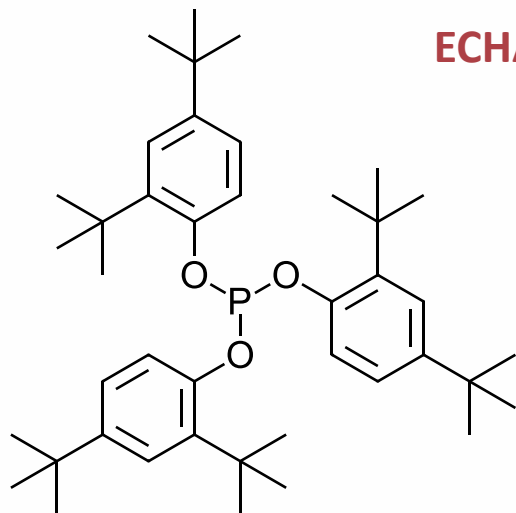
# Regulatory Challenges

What about starting materials and *in situ* degradation products?

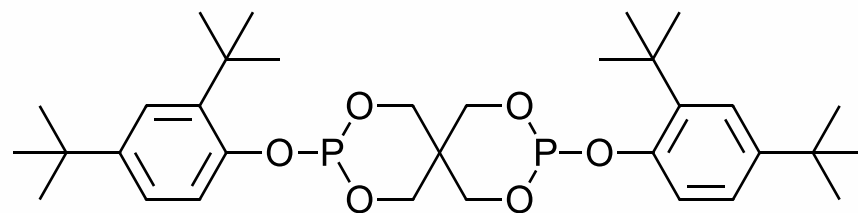


2,4-di-tert-butylphenol

ECHA CoRAP – Community Rolling Action Plan  
“Reproductive hazard” label?



AO-168

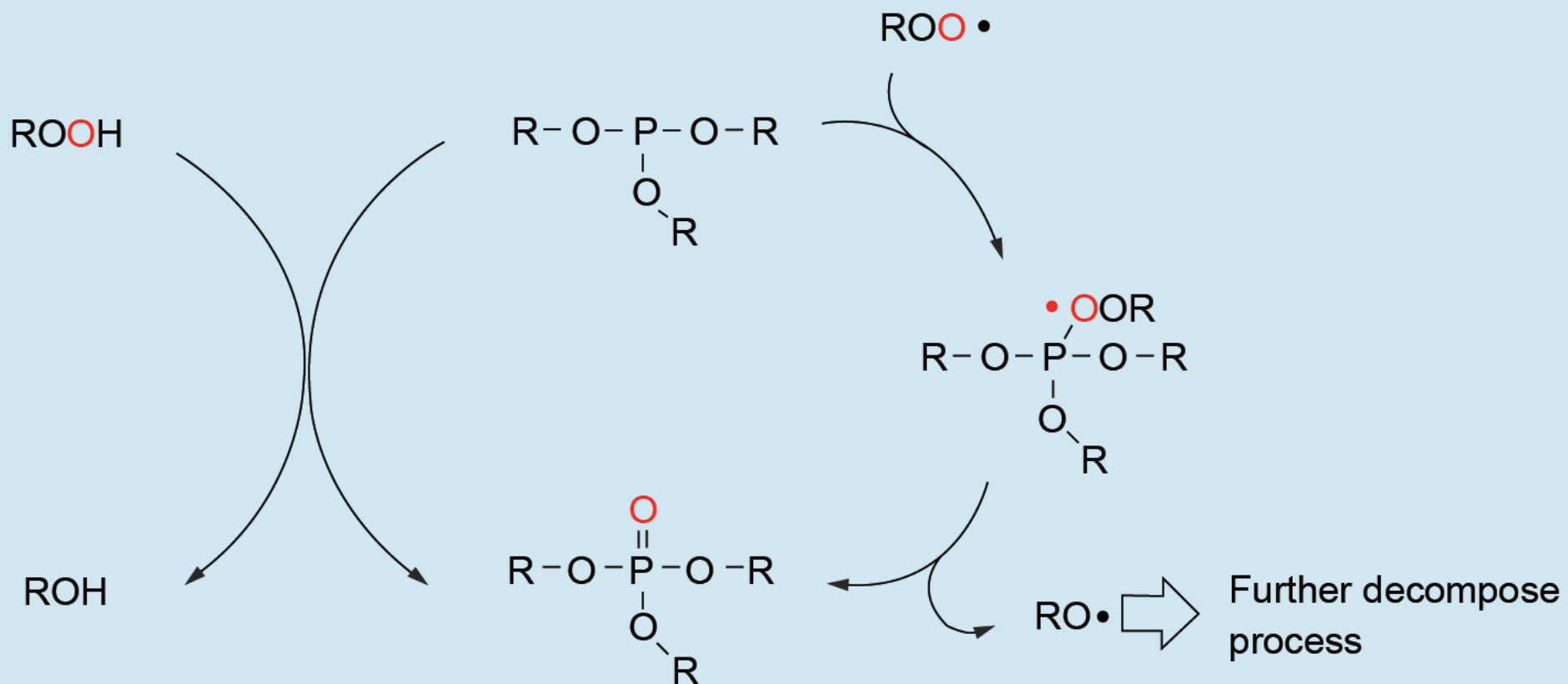


AO-626



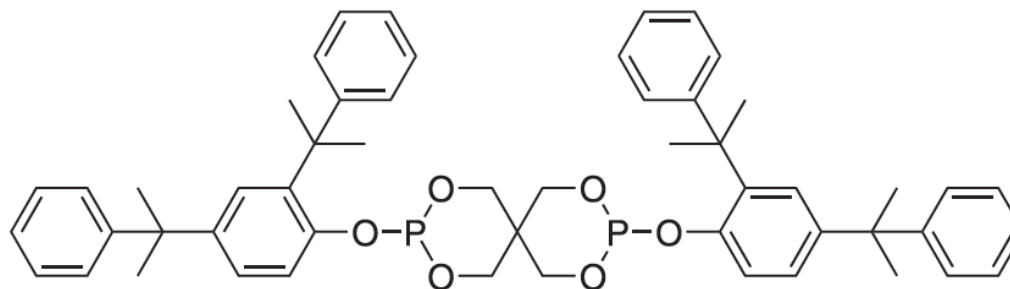
# Regulatory Challenges

Phosphites are “secondary antioxidants” that decompose hydroperoxides



# Regulatory Challenges

Alternate chemistries in the same class exist...



**AO-9228**

## Polypropylene melt flow data\*

	1st pass	5th pass
No phosphite	14	73
AO-168	11	42
AO-626	9	27
AO-9228	8	22

**Aggressive multipass – 280°C**

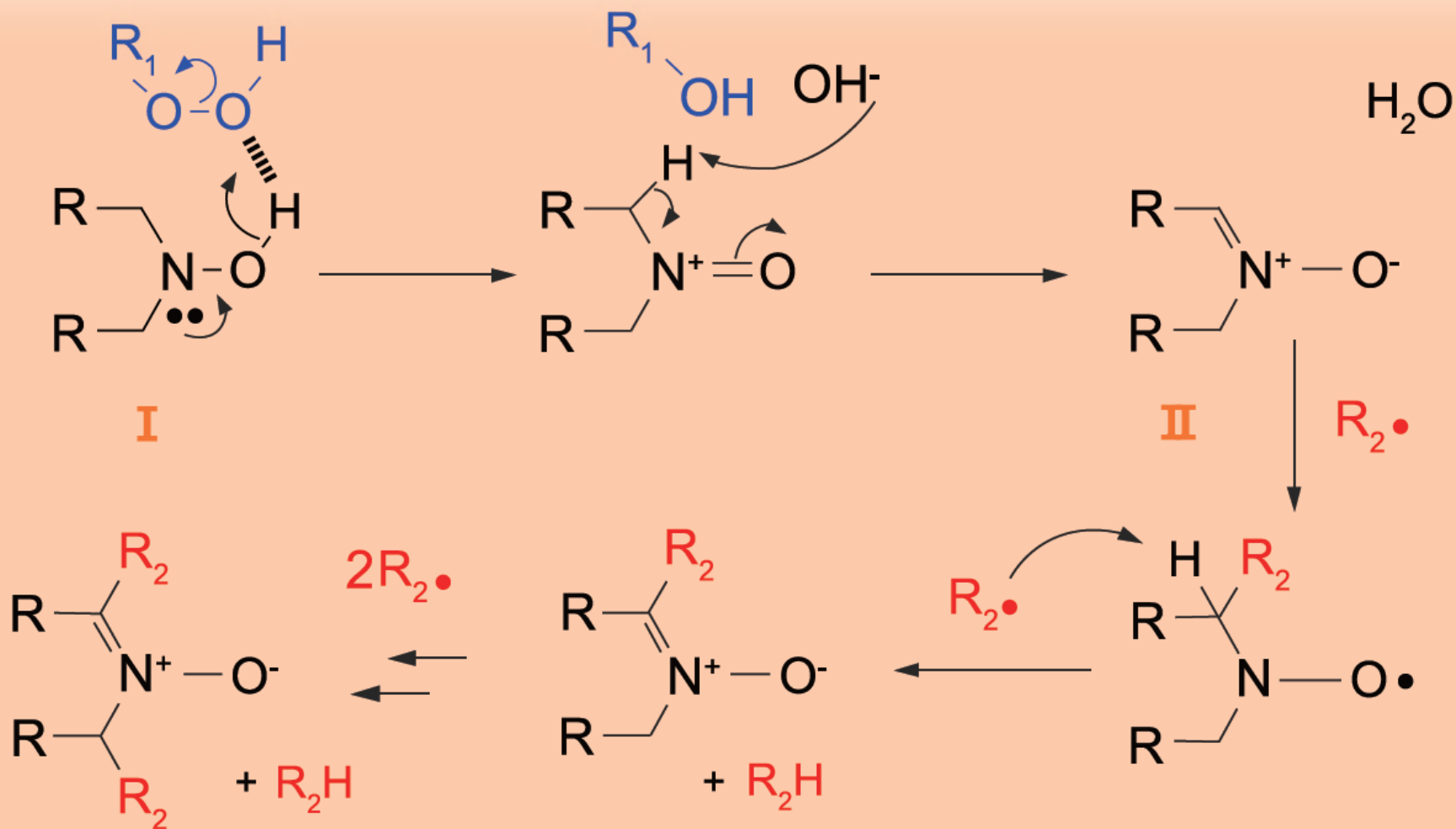
**500ppm phosphite**

**250ppm AO-1010**

**500ppm CaSt**

# Regulatory Challenges

...as well as entirely different chemical classes.



# Conclusions

Various threats to “business as usual” persist

- Supply shortages / price increases
- Regulatory challenges
  - Raw material shortages – “Blue Sky Initiative”
  - ECHA continues their work – will others follow?

## You have options

- Power to the formulator!
- Experiment, experiment, experiment!
- Partner with suppliers that see the “big picture”
  - Regulatory
  - Technical
  - “Plugged in” to global supply trends – and willing to share information

Manufacturers: Huge opportunity with expanded food contact approvals

# | Thank You For Your Time



**North American Specialty Chemical Distributor & Formulary Partner Since 1977**

Acknowledgments:

Scott Simmons

Jami Knoth

**Organizers and Moderators of SPE Polyolefins 2019**

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