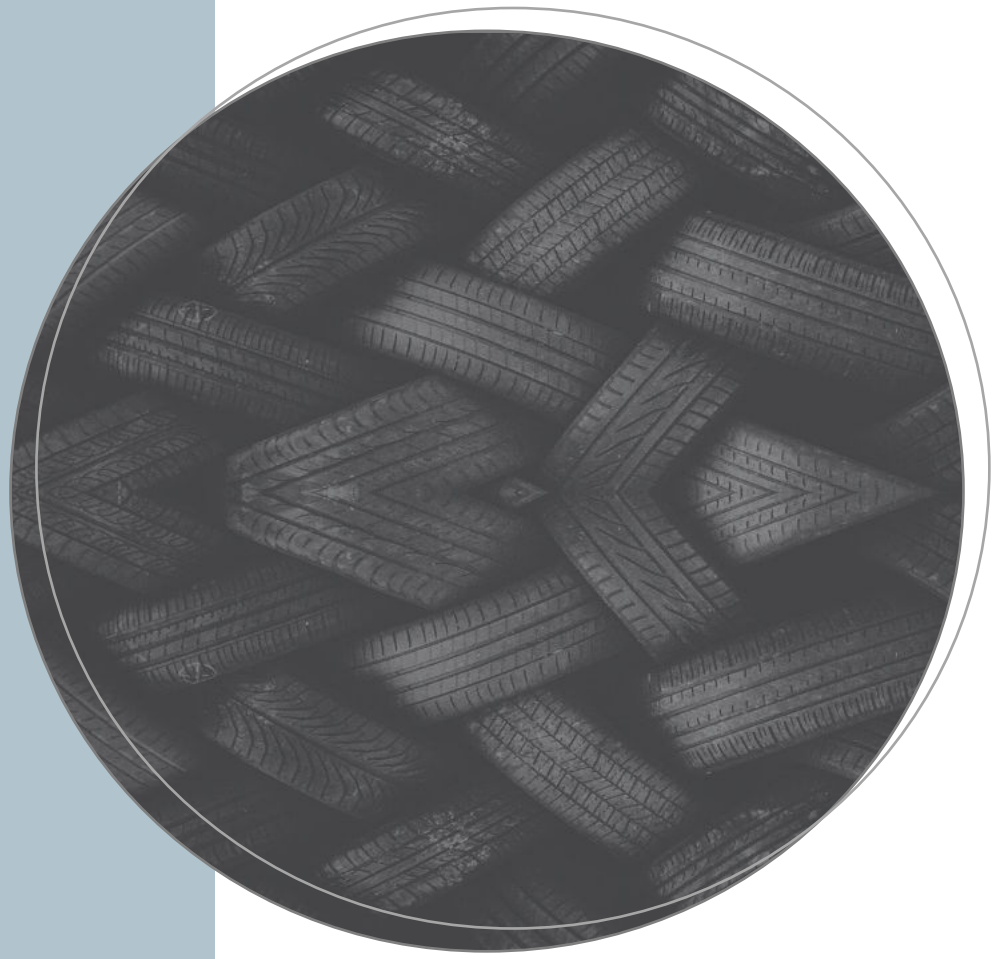
December 14, 2022

Collaborative Innovation Forum:
Functional Substitutes to 6PPD in Tires

What do we know about alternatives?



Aude Bechu,

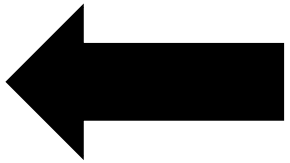
Sustainable Chemistry Catalyst

UMASS Lowell

Design options available

Change Bioavailability/Exposure

Change 6PPD Molecule



Focus of this presentation

Change Rubber Material

Change Tire Design

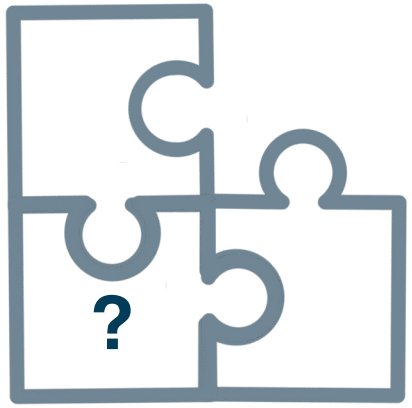
Antidegradant Alternatives have many functions

- Antiozonant
- Antioxidant
- Effective under stress
- Health and environmental safety

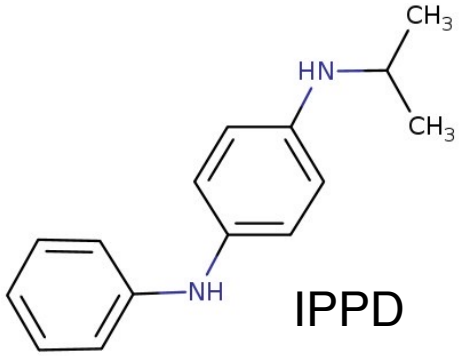
Focus area:

Known alternatives to 6PPD that have the potential to be implemented in **the short term**

Disclaimer: Information presented here was gathered from a literature and web search (public sources)

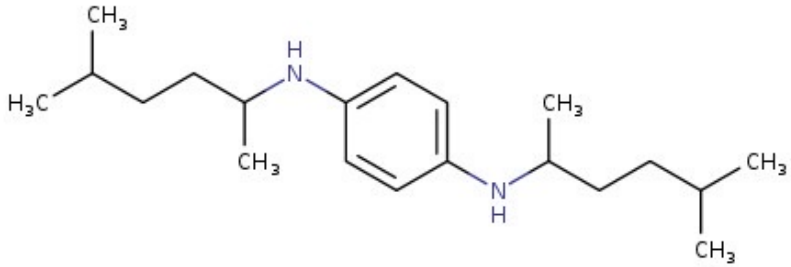


p-Phenylenediamines (PPDs)



IPPD

- 12 other PPD compounds found in literature research
- Range of size and antiozonant/antioxidant properties



77PD

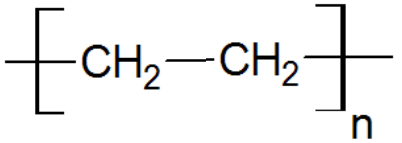
Known to have high aquatic toxicity and are skin sensitizers

Structures sourced from ECHA registry

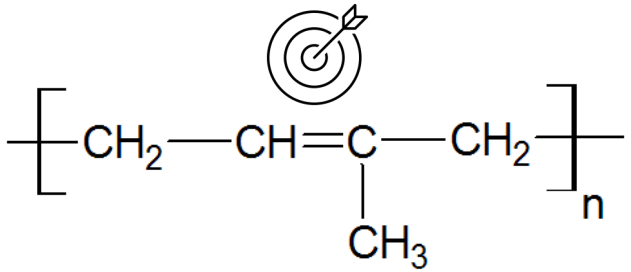
Limited antiozonants: Saturated bonds

- Microcrystalline wax
  - coating surface of tires
- Ethylene propylene diene rubber (EPDM)
  - integrated polymer granules into rubber

Saturated bonds

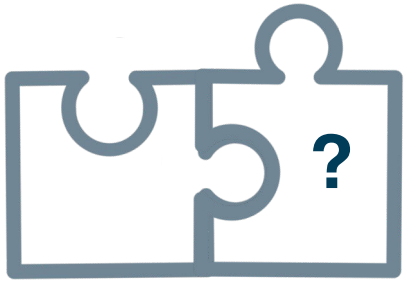


Natural rubber

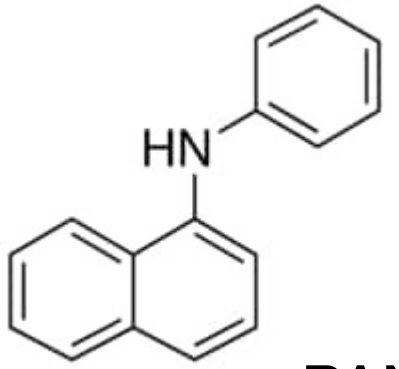


- Are not effective under stress (heat and mechanical conditions)
- Largely unknown toxicity

Structures sourced from Polymer Database

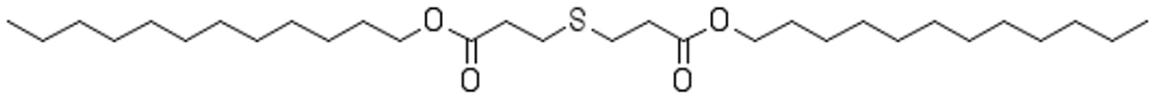


Many possible small molecule antioxidants



PAN

- Diarylamines (PAN)
  - Antioxidant under stress
  - Toxic to aquatic life and carcinogenicity concerns
- Thiodipropionates (DLTP)
  - Antioxidant for many elastomers
  - Some approved for food contact uses



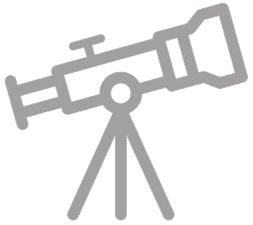
DLTP

Each small molecule class must be scrutinized individually and each will have different environmental transformations

Structures sourced from Millipore Sigma

Conclusion

- No silver bullet. Each current alternative has gaps in either performance or toxicity concerns.
- Currently we have two mechanisms to choose from to protect rubber: either sacrificial small molecule or large saturated structures.



6PPD alternatives must also adapt to future changes in tire composition and design

Survey of 6PPD alternatives for reference

Function	Compound class/ examples	Comments (performance or toxicity)
Antiozonant & Antioxidant	p-phenylamines, IPPD	Active under stress Toxic to aquatic life. Forms quinones in the environment
	p-phenylamines, 77PD	Active under stress Toxic to aquatic life. Quinone formation not yet investigated
Antiozonant (via saturated bonds)	Microcrystalline Wax	Not effective under stress Toxicity unknown
	Ethylene propylene diene rubber (EPDM)	Research-stage Toxicity unknown
Small molecule Antioxidant	Diarylamines, PAN	Active under stress Toxic to aquatic life and potential carcinogen
	Thiodipropionates, DTLP	General antioxidant for polymers Some approved for food uses