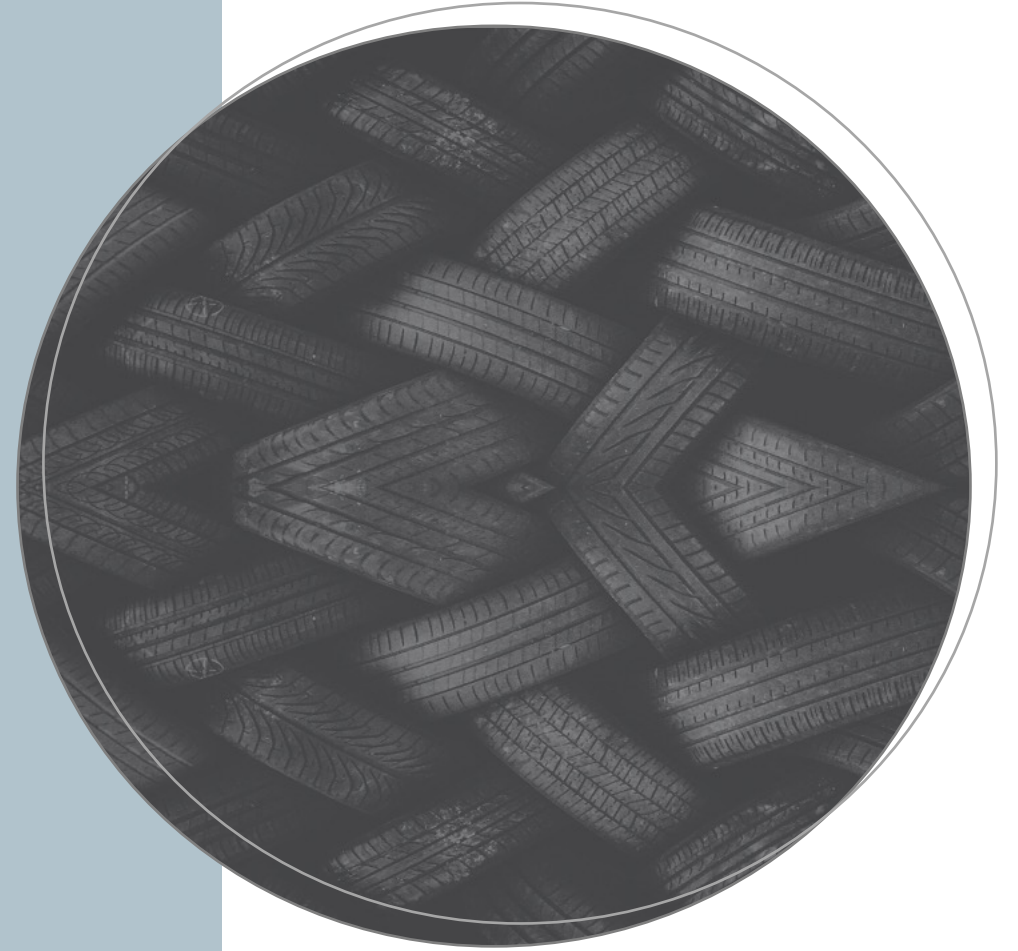


December 14, 2022

Collaborative Innovation Forum: Functional Substitutes to 6PPD in Tires

What do we know about alternatives?

Aude Bechu,
Sustainable Chemistry Catalyst
UMASS Lowell



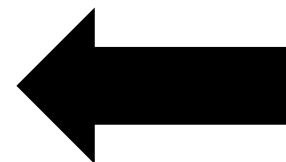
Design options available

Change Bioavailability/Exposure

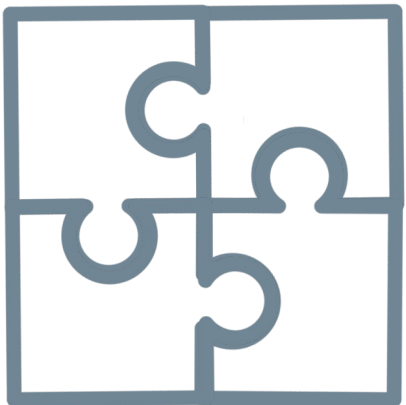
Change 6PPD Molecule

Change Rubber Material

Change Tire Design



Focus of this
presentation



Focus area:

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



Antidegradant Alternatives have many functions



- Antiozonant



- Antioxidant

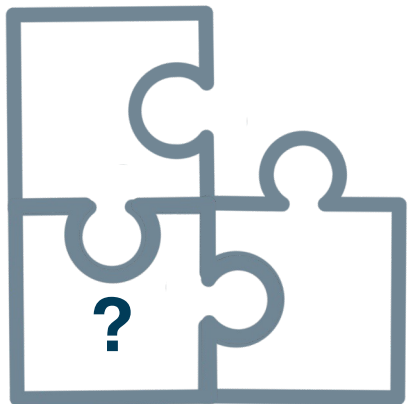


- Effective under stress



- Health and environmental safety

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

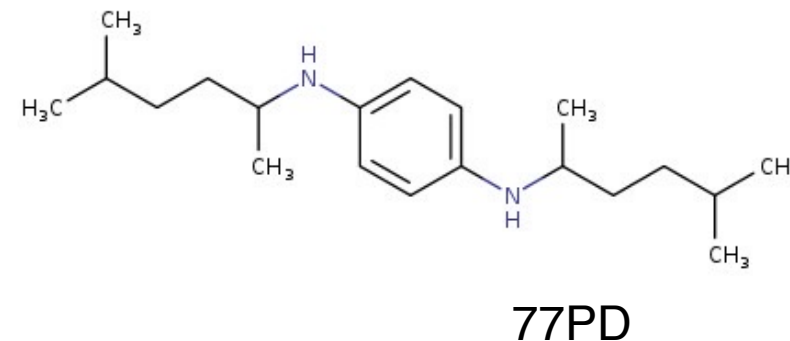
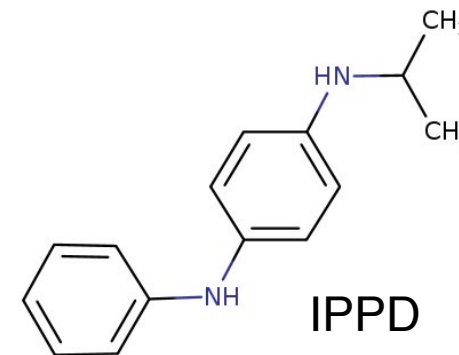


p-Phenylenediamines (PPDs)

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



Known to have high aquatic toxicity and are skin sensitizers



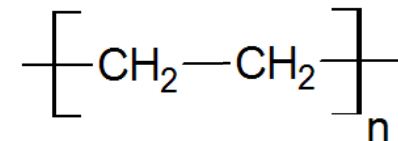
Structures sourced from ECHA registry



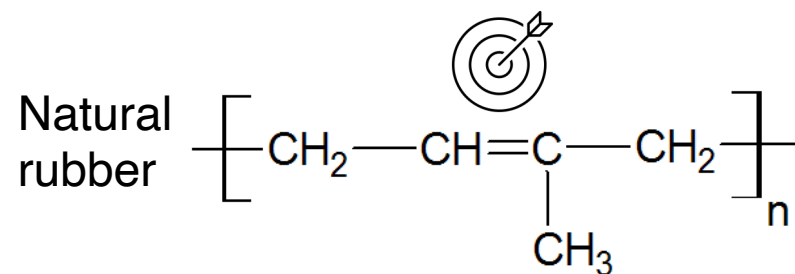
Limited antiozonants: Saturated bonds

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

Saturated
bonds



Natural
rubber

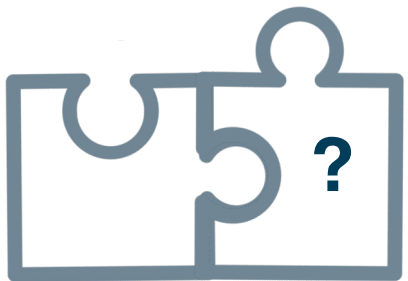


Are not effective under stress (heat and mechanical conditions)



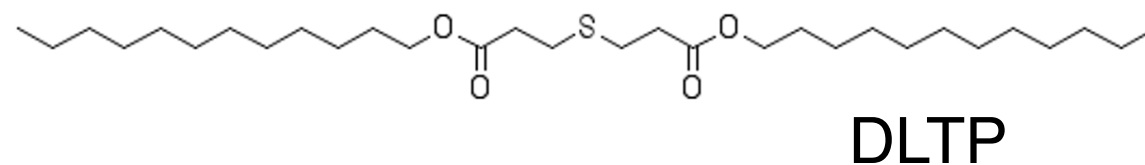
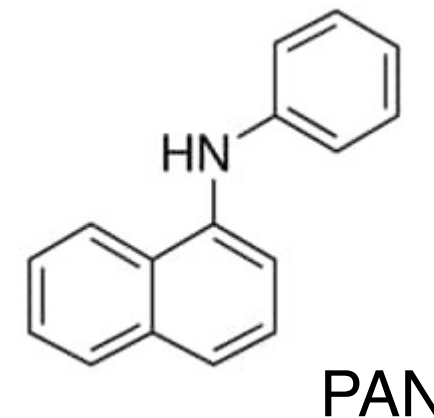
Largely unknown toxicity

Structures sourced from Polymer Database



Many possible small molecule antioxidants

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

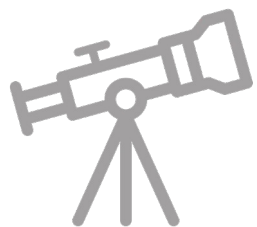


Each small molecule class must be scrutinized individually and each will have different environmental transformations

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 |