University of Massachusetts Lowell

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Collaborative Innovation Forum: Functional Substitutes to 6PPD in Tires

Meeting Report

February 2023

Sustainable Chemistry Catalyst

This Sustainable Chemistry Catalyst report is based on presentations and discussions that took place during the **Collaborative Innovation Forum: Functional Substitutes to 6PPD in Tires**, on December 14, 2022.

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- Saskia van Bergen, Marissa Smith and Craig Manahan (Washington State Department of Ecology)
- Kelly Grant, Anne Cooper Doherty, Topher Buck and Simona Balan (California Department of Toxic Substances)
- Chris Robertson (Polymer Technology Services LLC)

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The views expressed in this meeting report may not reflect the specific perspectives of every participant and participating organization but rather capture overarching themes from presentations and discussions.

ABOUT

Based at the Lowell Center for Sustainable Production (University of Massachusetts Lowell), The Sustainable Chemistry Catalyst is an independent research and strategy initiative that is focused on accelerating the transition to safer, more sustainable chemistry through research and analysis and stakeholder engagement with scientists, policymakers, and commercial actors.

Sustainable Chemistry Catalyst

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SUMMARY AND KEY TAKEAWAYS

N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine (6PPD), is an antidegradant widely used in automobile tires to protect rubber from degradation caused by ozone, oxygen, mechanical stress, and heat. When 6PPD reacts with ozone, it forms 6PPD-quinone. In 2021, researchers in Washington determined that 6PPD-quinone is highly toxic to coho salmon and a primary cause of urban runoff mortality syndrome (URMS).[a] In highly impacted watersheds, 40% to 90% of returning coho may die before spawning.[a] In 2022, research also revealed acute mortality concerns associated with exposure to 6PPD-quinone among additional salmonoids.[b]

Increasing evidence of 6PPD's significant adverse impact on aquatic species as well as potential regulatory actions are spurring activity to identify and commercialize safer and effective alternative tire antidegradants. On December 14, 2022, over 50 stakeholders including representatives from tire manufacturers, chemical suppliers, government agencies, university researchers, and NGOs participated in a *Collaborative Innovation Forum: Functional Substitutes to 6PPD in Tires*. The meeting was convened and facilitated by the Sustainable Chemistry Catalyst at the University of Massachusetts Lowell with support from the U.S. Environmental Protection Agency (U.S. EPA) through the Washington Department of Ecology. The purpose of the Forum was to identify collaborative needs and opportunities to expedite the identification, evaluation, and implementation of safer and effective alternatives (i.e., substitutes) to 6PPD.

The Forum addressed two aspects of tire safety:

- **Performance:** The effective performance of antidegradants in tires are critical. Tires are formulated and designed to ensure passenger safety and protect against tire shredding and failures, which could cause a vehicular accident. Passenger safety is paramount to tire performance and safety.
- **Toxicity:** Chemicals and materials have inherent hazard properties that relate to specific human and environmental health safety concerns. 6PPD confers concerns related to aquatic toxicity, which is the primary hazard property driving the need for an alternative antidegradant. However, there are other toxicity concerns associated with 6PPD such as skin sensitization, reproductive toxicity, among others.[c] The term safer alternative relates to the improved toxicity profile of alternative antidegradants compared to 6PPD.

Through presentations and discussion, Forum participants examined design considerations for alternatives to 6PPD, from both performance and toxicity perspectives. Participants brainstormed near and long-term actions to identify, evaluate and adopt alternatives to

[a] Tian et al. Science. 2021;371(6525):185–189. https://doi.org/10.1126/science.abd6951
[b] Brinkmann M, et al. Environ. Sci. Technol. Lett. 2022;9(4):333–338. https://doi.org/10.1021/acs.estlett.2c00050
[c] ToxServices LLC. N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine (CAS #793-24-8) GreenScreen® For Safer Chemicals Assessment. November 8, 2021.

6PPD in tires. A focus on collaborative opportunities to accelerate the pace of innovation was a continuous thread of discussion throughout the day.

Although the summary below captures Forum discussions, it may not reflect the specific perspectives of every participant and participating organization. Notable highlights and shared understandings resulting from the Forum are described below.

6PPD-quinione is highly toxic to coho salmon and other salmonoids. Concerns about the toxicity of 6PPD-quinone to salmonoids are only recently known and understood by researchers as well as the chemical and tire industries. 6PPD-quinone ranks as the 2nd most acutely toxic chemical to aquatic species ever evaluated, based on a comparison of LC_{50} levels (defined as the lethal concentration that kills 50% of test organisms) published by U.S. EPA.[d] As research continues investigating the environmental impacts of 6PPD and 6PPD-quinone, there was no disagreement among Forum participants regarding the significantly high aquatic toxicity of 6PPD-quinone and the pressing need to rapidly identify and adopt safer alternatives to 6PPD.

The use of antidegradants in tires is critical to passenger safety and tire longevity. Without an antidegradant, tires could fail within 100 to 1,000 miles of use.[e] 6PPD is highly effective at preventing degradation of the rubber material and hence tire failures such as blow outs, which is a significant threat to passenger safety. 6PPD is widely used by the industry because of its multifunctionality as an antidegradant – it is an effective antioxidant and antiozonant under stress.

Replacing 6PPD in tires is a complex substitution challenge. 6PPD is ubiquitous in tires. 6PPD is used throughout the tire in multiple components, including the sidewall, tread, and the rubber surrounding the internal steel belt. 6PPD was designed to migrate through the tire during manufacture and use. Tire tread and sidewall, unlike the inner steel belt, are parts of the tire where continued innovation is occurring. Components of the tire that are areas of continued optimization are more of a near-term opportunity for changes than those components that rarely change and where additional rigorous testing is required to provide assurances against catastrophic failures. Drop-in, "off the shelf" alternatives to 6PPD, such as other p-phenylenediamines (PPDs), can form quinones with unknown toxicity, further complicating substitution options.[f]

Having clear standards to support the design and testing of new antidegradants (including their transformation products) is critical. Standards exist for testing tire safety and performance and are primarily governed by federal agencies, such as the National Highway Traffic Safety Administration (NHTSA). However, standards are lacking for the human health and environmental impacts of antidegradants; there are no toxicological criteria nor requirements for a safer antidegradant in tires, which is needed to guide

[d] Tian et al. Environ. Sci. Technol. Lett. 2022;9(2):140–146. https://doi.org/10.1021/acs.estlett.1c00910
[e] Shaw et al. Rubber World. 1954;(130): 636-642.
[f] Cai et al. Environ. Sci. Technol. 2022;56(7):4142–4150. https://doi.org/10.1021/acs.est.1c07376

innovation activities, ensure acceptability by regulators and the marketplace, and avoid regrettable substitutions.

A range of research needs were identified to support innovation. Forum participants outlined a range of research needs to fill important knowledge gaps to support innovation. Primary needs include: (a) understanding the environmental transformation products associated with PPDs to inform predictive models and (b) understanding the distribution and release of 6PPD in tires to better focus on which component of the tire is responsible for environmental releases. In addition, use of a rational design approach was thought to provide a near-term opportunity to identify safer alternatives. This approach seeks to modify the parent compound of 6PPD or another PPD to negate the quinone formation as well as lessen the inherent toxicity impacts related to reproductive and acute aquatic toxicity, while preserving the antidegradant functionality. Some participants also noted that under the California Safer Consumer Products Program, the Department of Toxic Substances Control is expected to require an alternatives analysis be performed on 6PPD in tires (*note, this is currently in a proposal stage*).[g] This alternatives analysis would be executed by tire manufacturers and is expected to provide additional information regarding potential alternatives that will be made publicly available.

Use of tiered testing strategy will lessen the time and cost of innovation. The use of a tiered approach was recommended to reduce both cost and time resources, whereby potential alternatives could first be screened using existing toxicological data, including *in vitro* data. Different tiered pathways would likely be developed based on whether it is a new chemical or an existing chemical to improve efficiency and cost effectiveness of screening. Alternatives that demonstrate high concern for any endpoint on the minimum requirements list would be screened out and therefore "fail fast". Only a short-list of alternatives that show lower concern for toxicity (and meet material performance requirements) would then be subject to additional toxicological testing to fill critical data gaps. Developing a tiered testing strategy would clarify how both chemical companies and tire manufacturers, who must do separate tests to ensure antidegradant performance, can work together to accelerate safer chemical innovation.

A range of pre-competitive collaborative strategies exist to support and accelerate innovation. 6PPD substitution affects the chemical and tire industries. Accelerating development, commercialization, reformulation, and adoption of solutions will require collaboration between chemical suppliers and tire manufacturers, as well as regulators, academic researchers, tribal leaders, NGOs, and the entire value chain to develop, assess, and adopt alternatives. Forum participants discussed a range of collaborative approaches that have been used in other settings to support pre-competitive innovation activities in highly competitive industries. These include the use of pre-competitive data repositories such as those being used by the Pistoia Alliance, a collaboration of major pharmaceutical companies; use of innovation challenges designed and supported by industry partners[h]; and

[g] California Department of Toxic Substance Control. Safer Consumer Products Program. Proposed Priority Product: Motor Vehicle Tires Containing 6PPD Accessed January 2022.
[h] See more about the Pistoia Alliance here. Accessed January 2023.

joint testing platforms to share costs associated with the toxicological and performance testing of alternatives.

There was a clear commitment from Forum participants to work collaboratively to drive solutions that address the impacts being caused by the use of 6PPD in tires. The Forum itself helped to enhance understanding and trust across the multiple stakeholder groups in attendance, which is foundational to the viability of future collaborative efforts. At the close of the Forum there was a call to continue the effective dialog that began at the event and an expressed interest in collaborating in a pre-competitive environment to accelerate the pace of innovation of alternatives to 6PPD. Important next steps outlined include:

- **Define "safer" minimum toxicological criteria for alternatives to 6PPD to support the research and innovation processes.** This was a critical next step identified by Forum participants. There was a recommendation to use existing criteria for defining safer alternatives, such as Washington's Criteria for Safer,[i] as a starting point. Criteria need to address the issue of environmental transformation products and provide guidance regarding required test species for evaluating aquatic toxicity, including what evidence is sufficient to indicate that the toxicity of an alternative chemical is safer than 6PPD.

- **Fund pre-competitive multidisciplinary research to advance effective and safer alternatives to 6PPD.** The initial focus of research suggested by participants include:

    - Understanding 6PPD-quinone release from various components of the tire to improve predictive monitoring.
    - Integrating quinone transformations into rational design frameworks to reduce regrettable substitutions.
    - Integrating toxicity considerations into the antidegradant innovation pipeline to "fail faster," reducing investments in unsuccessful innovations.

  Developing solutions in the form of 6PPD alternatives should be the focus of research efforts. There was broad agreement that research teams involved in developing 6PPD alternatives should reach beyond material scientists, chemists, and chemical engineers to also include toxicologists, environmental engineers, and health scientists. A range of funding sources could be tapped to provide the support needed, including targeted funding from federal and state research programs, industry-supported research programs, and industry-academic research partnerships, among others.

- **Develop and advance specific collaborations to scale the pace of innovation.** Forum participants identified several specific collaboration ideas such as information-

[i] Washington State Department of Ecology. Regulatory Determinations Report to the Legislature: Safer Products for Washington Cycle 1 Implementation Phase 3. June 2022.

sharing tools, third party toxicity evaluation, and collaborative chemical safety and chemical performance testing programs. However, additional work by the chemical and tire industries is needed to focus and outline desired collaborative approaches, including goals, potential partners, coordination roles.

- **Explore establishing a voluntary commitment to phase out the use of 6PPD in tires by tire manufacturers, as a regulatory restriction has not been enacted**. Some stakeholders proposed that an explicit substitution goal and timeline would help increase and direct investment and capacity in the research and innovation processes on alternatives to 6PPD. The tire industry and chemical sector would have increased certainty and confidence in the industry-wide innovation need. Such a commitment would need to be guided by a clear roadmap for innovation, commercialization, and adoption of alternatives to 6PPD that outlines research, investment, and collaboration needs.

Replacing 6PPD in tires is a complex innovation challenge that requires balancing and optimizing performance, human and environmental health, and sustainability attributes. Participants walked away from the Forum understanding the challenges ahead but also generally recognizing a shared concern and the clear need for decisive action given the growing evidence of impact on a species of significant cultural, community, and economic value. The question discussed by participants was not one of whether 6PPD should be replaced but rather how to get there. Participants discussed the information, collaborations, and resources that will be needed to accelerate the pace of development, commercialization, and adoption of innovations that minimize impact to ecosystem and human health - while not compromising tire performance and passenger safety. Participants noted that building stronger and common understandings of goals, research needs, criteria, and measures of success can help guide resources and expedite actions to address the 6PPD challenge. The positive, open, and engaged discussions and feedback from the Forum provide evidence that the "collaborative innovation"[j] approach can play an important role in addressing current and future chemical challenges in a pre-competitive space where pressures to act are elevated.

[j] Becker M, Tickner JA. Sustainable Chemistry and Pharmacy. 2020;18:100330. https://doi.org/10.1016/j.scp.2020.100330

1. INTRODUCTION

In 2021, researchers in Washington identified that a transformation product of N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine (6PPD), 6PPD-quinone, is highly toxic to coho salmon at critical life stages and a primary cause of urban runoff mortality syndrome (URMS).[1] In highly impacted watersheds, 40% to 90% of returning coho die before spawning.[2] In 2022, research also revealed acute mortality concerns associated with exposure to 6PPD-quinone among several trout species in lab tests.[3]

URMS was documented in the early 2000s, during routine salmon habitat restoration projects from the 1990s,[4] but only recently has URMS been linked to 6PPD-quinone. Salmon play an integral part of religion, culture, and physical sustenance of Pacific Northwest Tribal Nations. This critical species is endangered and/or threatened under the Endangered Species Act in regions across the U.S. west coast.

Based on existing evidence, 6PPD is classified as a Category 1 acute aquatic toxicant, the most hazardous aquatic toxicity classification under the Globally Harmonized System (GHS) for the Classification and Labelling of Chemicals.[5] 6PPD is also a skin sensitizer and classified as a GHS Category 1B reproductive toxicant as it can prolong gestation and has been shown to cause difficult or obstructed labor in rats.[6]

6PPD is an antidegradant, a chemical additive widely used in the tire industry to protect rubber from degradation caused by ozone, oxygen, mechanical stress, and heat. Preventing tire degradation is critical to both passenger safety and tire longevity. According to the U.S. Tire Manufacturer's Association (USTMA), all members use 6PPD in tires. They note that rubber without 6PPD could "decrease the structural integrity of the tire and risk catastrophic passenger safety issues."[7]

Despite the widespread and critical use of 6PPD in tires, the recently understood significant adverse impacts of 6PPD-quinone on aquatic species is driving urgent action to identify and commercialize safer and effective alternative tire antidegradants.

On December 14, 2022, over 50 stakeholders including representatives from tire manufacturers, chemical suppliers, government agencies, university researchers, and non-governmental organizations (NGOs) participated in a *Collaborative Innovation Forum: Functional Substitutes to 6PPD in Tires*. The meeting was convened and facilitated by the

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[1] Tian et al. Science. 2021;371(6525):185–189. https://doi.org/10.1126/science.abd6951
[2] Feist BE, et al. Ecol Appl. 2017;27:2382-2396. https://doi.org/10.1002/eap.1615
[3] Brinkmann M, et al. Environ. Sci. Technol. Lett. 2022;9(4):333–338. https://doi.org/10.1021/acs.estlett.2c00050
[4] Scholz NL et al. PLoS ONE, 2011;6(12). https://doi.org/10.1371/journal.pone.0028013
[5] Manahan, C. Technical Memo: Assessment of potential hazards of 6PPD and alternatives; Washington State Department of Ecology, Washington, 2021; ToxServices LLC. N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine (CAS #793-24-8) GreenScreen® For Safer Chemicals Assessment. November 8, 2021.
[6] ToxServices LLC. N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine (CAS #793-24-8) GreenScreen® For Safer Chemicals Assessment. November 8, 2021; European Chemicals Agency. N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine Registration Dossier. European Union, 2022.
[7] USTMA 6PPD and Tire Manufacturing. Accessed January 2023.

Sustainable Chemistry Catalyst at the University of Massachusetts Lowell with support from the U.S. Environmental Protection Agency (U.S. EPA) via the Washington Department of Ecology. The purpose of the Forum was to identify collaborative needs and opportunities to expedite the identification, evaluation, and implementation of safer and effective alternatives to 6PPD. The Forum focused on opportunities to identify and accelerate alternatives to 6PPD in tires; it did not focus on characterizing the magnitude of the impacts associated with environmental exposures to 6PPD nor did it delve into other solution strategies, such as on-site mitigation options. In addition, the Forum did not focus on the specific merits of certain alternatives due to the proprietary nature of chemical development. Specific alternatives were only mentioned to set the scene for stakeholders who may not be familiar with the multifunctionality of 6PPD.

Specific desired outcomes of the Forum included:

- Understanding the current context of alternatives to 6PPD in tires, from both a toxicological and performance perspective.
- Discussing critical design considerations to support the innovation of safer and effective alternatives for the function of 6PPD in tires.
- Exploring near- and long-term needs and opportunities associated with the commercialization of safer and effective alternatives to 6PPD in tires.
- Identifying collaboration opportunities and next steps to advance innovation activities for the functional substitution of 6PPD in tires.

This meeting report provides an overview of presentations and participant discussions with a focus on next steps and needs. Although this summary of the meeting is an accurate reflection of the Forum discussions, it may not reflect the perspective of every participating individual or organization. The organizations of the participants are listed in **APPENDIX A** to show who was represented in the conversations. The Forum agenda is included in **APPENDIX B**.

2. SETTING THE CONTEXT

The Forum began with five formative presentations aimed at setting context and common ground for later discussions. The first two presentations outlined background information on 6PPD, from both a tire industry perspective and an environmental health perspective. The following two presentations provided participants with an overview of potential alternatives to spur discussions about design considerations. The last presentation delved into how to think about alternatives and substitution processes.

6PPD: the problem

Edward Kolodziej, University of Washington

Dr. Kolodziej's presentation outlined the broad scientific consensus that has been reached regarding the toxicity of 6PPD-quinone and its ubiquitous presence in the environment. Multiple independent groups had replicated results showing that the coho LC_{50} (defined as the lethal concentration that kills 50% of test organisms) of 70-130 ng/L and had demonstrated that other sensitive species exist, such as brook trout and rainbow trout. Although it was acknowledged that not all aquatic species are as sensitive to 6PPD-quinone as coho salmon, it is important to note how potently toxic 6PPD-quinone is – it ranks among the most toxic to aquatic species based on comparisons of LC_{50} levels published by U.S. EPA.[8] Lastly, the ubiquitous nature of tire-derived contaminants, including 6PPD-quinone, was presented; recent scientific studies point to the presence of 6PPD, 6PPD-quinone, as well as other PPDs and their quinones in the air (as $PM_{2.5}$), in household dust, and in human urine.[9]

A tire industry perspective on 6PPD replacement: the challenge

Chris Robertson, Polymer Technology Services LLC

Dr. Robertson's presentation helped to provide participants with foundational information about antidegradants in tires. The complex structure of tires was outlined – from the internal belts and plies that are rubber coated to the outer tread and sidewall. The 6PPD content of each of the rubber-based components is 0.5-1.5 wt%. The potential to confine 6PPD to specific areas in the tires and therefore completely limit its release into the environment was discounted due to the migration of the compound throughout these different components, both during the production and use of the tire. Once the compound migrates to the tire surface, it can continually act as a sacrificial molecule to protect the rubber against ozone and oxygen in both static and dynamic conditions. The migration, or blooming, of 6PPD to the surface of the tire is critical to its performance. Tires without any 6PPD (or comparable antidegradant) were demonstrated to have visible cracks and therefore lower performance. Dr. Robertson also alluded to growing sustainability efforts in the tire industry. If a substitute antidegradant was less effective (i.e., reduced product life) then there would be negative impacts on the tires' sustainability profiles. There is also a risk of litigation related to tire failure.

What do we know about the alternatives - literature perspective

Aude Bechu, UMass Lowell

Dr. Bechu's presentation shifted to possible solutions and what was known about their performance and toxicological profiles. Chemical substitution is just one design solution; material (rubber) change and tire redesign were also identified as possible, though more complex, options (**FIGURE 1**). These approaches regarding a solution consistently focus on

[8] Tian et al. Environ. Sci. Technol. Lett. 2022;9(2):140–146. https://doi.org/10.1021/acs.estlett.1c00910; Erratum in: Science. 2022;375(6582):eabo5785.

[9] Du et al. Environ. Sci. Technol. Lett. 2022;9(12):1056-1062. https://doi.org/10.1021/acs.estlett.2c00821; Zhang et al. Environ. Sci. Technol. Lett. 2022;9(5):420-425 https://doi.org/10.1021/acs.estlett.2c00193; Wang et al. Environ. Sci. Technol. 2022;56(15):10629-10637 https://doi.org/10.1021%2Facs.est.2c02463.

function of either the product or the chemical. 6PPD's primary function in tires is as an antiozonant and antidegradant. Substituted p-phenylenediamines (PPDs), for which researchers have found 14 examples, are the simplest substitute due to their similarity in structure. However, their performance may differ from 6PPD, and their use could lead to similar concerns about environmental transformations, aquatic toxicity, skin sensitization, and reproductive toxicity. Using saturated bonds, such as microcrystalline wax, as an antiozonant, was noted, but these chemicals are not effective under dynamic conditions and have unknown toxicity concerns. Lastly, small molecule antioxidants were presented, but their small size and reactivity means that the potential for release and environmental transformation are high. There are no immediately available alternatives to replace 6PPD, as data gaps remain related to both tire performance and toxicity.

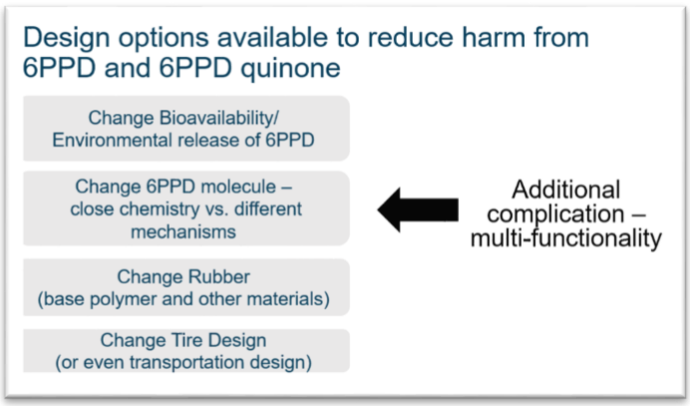

FIGURE 1: Design options available for substitution of 6PPD in tires, with complexity and timeframe increasing from changing bioavailability to changing tire design.

What do we know about the alternatives - patent perspective

Miles Dearth, ACE Laboratories

Dr. Dearth presented on key findings from a recent patent search for 6PPD alternatives. Keyword searches, such as ozone and tread were necessary to narrow down the thousands of patents in this space. Certain patents for antidegradants were also expired, pointing to the potential for quick uptake by other companies. Dr. Dearth narrowed in on a recent patent that pointed out longer lasting antiozonants. The authors had substituted many functional groups on the PPD core molecule. This example of innovation highlighted the possibility for rational design of the next generation of antidegradant chemicals.

How to think about substitution

Joel Tickner, UMass Lowell

Dr. Tickner discussed approaches to chemical substitution. He noted that both finding an adequate substitute and the widespread adoption of the alternative could present their own challenges. The method of alternatives assessment (defined as a "process for identifying, comparing, and selecting safer alternatives to chemicals of concern – including those used in materials, processes, or technologies – on the basis of their hazards, performance, and economic viability"[10]) and the concept of functional substitution[11] provide a clear process for identifying a safer alternative. Rational design, which neutralizes toxic parts of chemicals while maintaining function, was another route for generating alternatives. Dr. Tickner gave examples of other industries, such as antifouling coatings on boats as well as fire suppression, that had innovated by focusing on function, design, and overcoming problems unique to their industries. These examples make a case for fit-for-performance functionality to potentially expand performance standards that may have been built specifically with 6PPD (or a similar compound) in mind. Lastly, safe and sustainable by design efforts in Europe were identified to stress that chemical safety is coming to the front of future design processes for sustainability.

3. EXPLORING CRITICAL DESIGN CONSIDERATIONS. WHAT IS SUFFICIENT PERFORMANCE? WHAT IS SAFE ENOUGH?

Alternatives to 6PPD will need to meet specific standards related to the performance of the tire as well as address human health and environmental concerns. The Forum addressed two aspects of tire safety:

- **Performance:** The effective performance of antidegradants is critical for passenger safety to protect against tire shredding and failures, which could cause a vehicular accident. Passenger safety is paramount to tire performance and safety.
- **Toxicity:** Chemicals and materials have inherent hazard properties that relate to specific human health and environmental concerns. 6PPD as an antidegradant in tires confer safety concerns related to aquatic toxicity, which is the primary hazard property driving the need for an alternative antidegradant. However, there are additional toxicity concerns associated with 6PPD such as skin sensitization, reproductive toxicity, among others.[12] The term safer alternative relates to the improved toxicity profile of alternative antidegradants compared to 6PPD.

The goal of this session was to begin a discussion regarding key design considerations that alternatives to 6PPD need to demonstrate in terms of performance as well as toxicological criteria to define a safer determination (see below for definitions). Three formative presentations provided considerations that participants explored further in small group discussions.

[10] U.S. National Research Council. 2014. A Framework for the Selection of Chemical Alternatives.
[11] Tickner JA, et al. Environ Sci Technol. 2015;49(2):742-9. https://doi.org/10.1021/es503328m
[12] ToxServices LLC. N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine (CAS #793-24-8) GreenScreen® For Safer Chemicals Assessment. November 8, 2021.

Performance requirements for antidegradants in tires: Laboratory Scale

Erick Sharp, ACE Laboratories

Mr. Sharp described how the performance requirements of antidegradants become increasingly complex as rubber moves through the supply chain into tires. As a baseline, an antidegradant cannot interfere with the other chemicals and materials that are mixed into rubber base polymer. Next, the complex material that is commonly referred to as rubber is synthesized through vulcanization, which creates sulfur bridges between rubber polymer molecules. This process is assessed by rheology, which measures the increasing strength of rubber during the vulcanization process. From there, small rubber samples can be made and tested for a variety of properties which indicate potential for tire application, including viscosity, abrasion, flex, fatigue, static and dynamic ozone resistance. This battery of performance tests on small rubber samples can also be extended to analytical tests where crumb rubber, wash water, and surface wipes can be evaluated for leaching of antidegradants and their transformation products. These tests are supportive of a "fail fast" process to narrow-in quickly on a short-list of potential antidegradants that warrant more extensive product testing.

Performance requirements for antidegradants in tires: Product Scale

Bruce Lambillotte, Smithers

Mr. Lambillotte provided a brief overview on some of the tests conducted on whole tires. Once an antidegradant passes testing in small rubber samples, it must be tested in tires themselves. Tire tests relevant to demonstrating the performance of an antidegradant include dynamic ozone, traction tests (dry, wet, snow, and ice) as well as durability and endurance testing. Oxygen is able to migrate through tires, while ozone attacks are concentrated at the tire surface. However, ozone damage propagates into the tire due to chain scission, which causes multiple double bonds to break due to one molecule of ozone.

Reflections from USTMA

Jamie McNutt

Ms. McNutt echoed that there are tire-specific requirements for performance which cannot be easily modelled on small rubber samples. For example, tires must support the weight of the vehicle, perform in a variety of conditions, and last years. There are also NHTSA motor vehicle safety standards that the product must meet. These standards were strengthened following a series of incidents of tire failure. The complex nature of the tire also demands that 6PPD act as an antiozonant on the surface of the tire to prevent the formation of cracks (**FIGURE 2**), but an also acts as an antioxidant and a free-radical scavenger throughout the tire as well. There are many steps and tests required to evaluate potential alternatives in a tire. USTMA provided an overview of the various steps and testing during their presentation. Preliminary steps and testing would include assessment of dynamic ozone crack resistance and chemical compatibility. If potential materials do not pass this initial screening process, they would not move forward for further testing and evaluation. If potential materials pass this initial screening for all required properties, further evaluation must be conducted by tire manufacturers. The unique proprietary formulas of the tire manufacturers create a condition in which 6PPD alternatives would need to be tested by each company to ensure tire safety and performance. Test criteria for the evaluation of tire safety and performance is understood by the tire industry; the current limitation is the lack of clarity on the toxicity criteria.

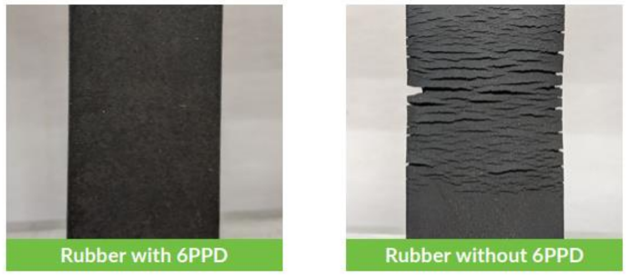

FIGURE 2: Rubber with and without 6PPD. Source: US Tire Manufacturer's Association[13]

Small Group Discussions - Sufficient Performance?

Working in small groups, participants discussed performance parameters for antidegradants to support the innovation process. Participant discussions highlighted that passenger safety and performance of tires are important not only to the tire industry, but to all stakeholders.

The need for antidegradants in tires was clear. If tires did not have an antidegradant, tires could fail within 100 to 1,000 miles of use.[14] Participants agreed that tire safety and associated performance must be maintained, and some stakeholders indicated that there might be flexibility regarding how this performance is achieved as the material formulation changes.

Although formative presentations at the Forum outlined some of the testing standards used, there are even more tests that tire manufacturers perform to ensure antidegradants in tires function as needed. There are standards that are specific to given regions, for example standards set by the NHTSA in the U.S. versus standards set by the European Commission.[15] There was a recommendation to develop shared language and agreement on the use of specific testing standards beyond those dictated by government agencies so than any research group testing, for example sidewall cracking resistance, would be able to assess performance using the same standards.

While some participants questioned whether specific standards over-specify performance needs (e.g., cracking resistance), in the U.S. these have been established by NHTSA and any discussion regarding their appropriateness would need to be discussed with the agency. When asked whether tires are currently over-engineered regarding some performance standards related to antidegradant functionality, the response in the group was "no," especially given the cost-competitive environment faced by tire manufacturers,

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[13] US Tire Manufacturers Association. Supporting Research Into 6PPD and 6PPD-Quinone. Accessed January 2023.
[14] Shaw et al. Rubber World. 1954;130:636-642.
[15] Regulation (EC) No 661/2009

continued liability concerns, and given that tires need to be designed with a broad range of use conditions and users in mind. However, participants noted that the standards are based on overall performance. Although 6PPD is not specifically required by Federal Motor Vehicle Safety Standards (FMVSS), tire manufacturers would never build a conventional tire without use of antidegradants and the high performance of 6PPD has made it the default antidegradant used by most tire manufacturers.

Participants from tire manufacturers also emphasized that their customers care most about tire durability and endurance. Further, given concerns about end of life of tires, a potential alternative that decreases tire longevity would increase tire waste.

Over the decades, there has been continued innovation within the tire industry resulting in a paralleled evolution in tire performance. Participants acknowledged however that what is missing in current innovation processes are the toxicity considerations related to 6PPD throughout the process. A major hinderance in identifying alternatives to 6PPD are standards not related to performance, but expectations related to toxicity.

Current practices for making a "safer" determination

Molly Jacobs, UMass Lowell

Ms. Jacobs's presentation began by acknowledging that the goal is to design products and processes that are inherently benign by design. However, a key question regarding alternatives to 6PPD relates to what toxicological criteria need to be met to be "safe enough?" The presentation reviewed three examples of guidelines for deciding as to whether the toxicity of a given alternative is safer, including:

- Organization for Economic Cooperation and Development's (OECD's) "Guidance on Key Considerations for the Identification and Selection of Safer Chemical Alternatives"[16]
- Safer Products for Washington program "Appendix C: Criteria for Safer"[17]
- Sustainable Chemistry Catalyst's "Criteria for Safer: Alternatives to Aqueous Film Forming Foam Products"[18]

Alignment on minimum toxicological criteria for making a safer alternative determination centered on ensuring there is evidence to support no high concern related to carcinogenicity, mutagenicity, reproductive toxicity, developmental toxicity, acute and chronic aquatic toxicity, persistence, and bioaccumulation. GreenScreen® was identified as a hazard assessment tool that requires identification and evaluation of environmental transformation products in addition to the parent compound.

[16] OECD. Guidance on Key Considerations for the Identification and Selection of Safer Chemical Alternatives. 2021.
[17] Washington State Department of Ecology. Regulatory Determinations Report to the Legislature: Safer Products for Washington Cycle 1 Implementation Phase 3. June 2022.
[18] Sustainable Chemistry Catalyst. Criteria for Safer: Alternatives to Aqueous Film Forming Foam Products. 2022.

Small Group Discussions – Safe Enough?

Working in small groups, participants discussed considerations for making a safer determination associated with the toxicity profile of alternatives to 6PPD in tires. One group suggested adopting existing approaches that address minimum requirements for making a safer determination. For example, the Criteria for Safer that are currently being used by Washington Department of Ecology/Health to implement the Safer Products for Washington Law is outlined in **TABLE 1**. These criteria include human health endpoints such as carcinogenicity, mutagenicity, reproductive toxicity, as well as persistence, bioaccumulation and acute/chronic aquatic toxicity and are based on standardized testing and assessment methods outlined in the Globally Harmonized System (GHS) for the Classification and Labeling of Chemicals.

Hazard Endpoint	Requirement
Carcinogenicity	Required
Mutagenicity/Genotoxicity	Required
Reproductive or Developmental Toxicity	Required
Endocrine Disruption	Not required
Acute Toxicity	Not always required*
Single or Repeat Systemic Toxicity	Not always required*
Single or Repeat Neurotoxicity	Not always required*
Skin or Respiratory Sensitization	Required
Skin or Eye Irritation	Not required
Acute or Chronic Aquatic Toxicity	Required
Persistence	Required
Bioaccumulation	Required

Notes:

- * = Two out of these three endpoints require data.

TABLE 1: Minimum Data Requirements and Potential Exemptions – Criteria for Safer, Safer Products for Washington, June 2022

Participants discussed a growing need to consider the human toxicological impacts from 6PPD and 6PPD-quinone given that exposure concerns have been documented – a recent study shows high frequency of detection in human urine and even higher concentrations among pregnant women,[19] which elevates the importance of addressing endpoints such as reproductive/developmental toxicity.

With regards to addressing aquatic toxicity, participants discussed how to approach tests for coho salmon given that the species is not the focus of standardized test models for assessing chemical toxicity. The use of a tiered approach was recommended to reduce both cost and time resources, whereby potential alternatives could be screened using existing test data and which could be generated quickly though *in vitro* tests. Alternatives that demonstrate high concern for any endpoint on the minimum requirements list would be screened out; participants used the term "fail fast" in that only a short-list of alternatives that show low concern for toxicity would then be subject to additional critical experimental testing, such as

[19] Du B, et al. Environ. Sci. Technol. Lett. 2022;9(12):1056–1062. https://doi.org/10.1021/acs.estlett.2c00821

tests specific to coho salmon, which can be costly since they are not considered among the routine battery of tests used for aquatic testing. Participants did however recognize that rainbow trout (*Oncorhynchus mykiss*) is the focus of standardized test methods for aquatic toxicity and this species has also shown sensitivity to 6PPD in research by Brinkmann and colleagues.[20] In addition, studies conducted in the 1990s examining the toxicity of tire leachate did demonstrate that exposure causes acute mortality to rainbow trout.[21] Gill cell lines (but not liver cells) of the rainbow trout showed sensitivity to 6PPD-quinone, demonstrating the potential of use of quick and relatively inexpensive *in vitro* tests.[22]

Although there was no determination during the meeting regarding what aquatic toxicology tests should be performed to capture sensitivity to the broadest array of species, there was a recommendation to consider those specified by U.S. EPA's Office of Water Quality, which dictates test parameters for 8 aquatic organisms, including rainbow trout. These test parameters are more comprehensive than those identified under the Toxic Substances Control Act (TSCA). For new chemicals submissions under TSCA, there are no specific tests required.

The importance of considering environmental justice (defined by the U.S. EPA as, "the fair treatment and meaningful involvement of all people regardless of race, color, national origin, or income with respect to the development, implementation and enforcement of environmental laws, regulations and policies"[23]) was identified during discussion in one working group. In the case of 6PPD, loss of coho and other salmonids is having negative consequences on the health, economy, and culture of Tribes and Tribal members. These communities are also vulnerable to toxic burdens carried in coho and other fish given that diets are highly dependent on fish consumption. Assessment of alternatives need to consider impacts to vulnerable populations, including pregnant women and children who are more sensitive to the impacts of toxic chemicals, as well as disproportionately impacted communities.

As 6PPD-quinone is formed by a reaction between 6PPD and ozone in the environment, and certain classes of antiozonants additives are designed to be reactive, the group discussed how environmental transformation products should be considered when evaluating alternatives. Existing uncertainties regarding the formation of toxic transformation products creates additional complexities for the substitution process. Washington's Criteria for Safer requires that all known breakdown/transformation products also meet its minimum criteria for safer.

Participants suggested using rational design. Rational design is defined as the creation of similar new molecules with a specific functionality, while designing out the toxicity, based upon the ability to predict how changes to the molecule's structure will affect its behavior (through physical models), to better understand the type of transformation products expected and to minimize the likelihood of toxic chemicals being formed. Some participants noted that

[20] Brinkmann M, et al. Environ. Sci. Technol. Lett. 2022;9(4):333–338. https://doi.org/10.1021/acs.estlett.2c00050
[21] Day KE, et al. Chemosphere. 1993;27(4):665-675. https://doi.org/10.1016/0045-6535(93)90100-J
[22] Brinkmann M, et al. Environ. Sci. Technol. Lett. 2022;9(9):765–771. https://doi.org/10.1021/acs.estlett.2c00431
[23] U.S. Environmental Protection Agency. Environmental Justice. Accessed January 2023.

currently computational toxicology data do not accurately predict 6PPD-quinione as a principal transformation product. As such, the group agreed that more data is needed as inputs to improve environmental fate predictions of PPDs and other alternatives. One group also believed that if an alternative demonstrates low concern for toxicity across multiple endpoints, the likelihood that it will transform to toxic byproducts will be reduced.

Some participants discussed the need for greater certainty (i.e., "cannot have the goal post move on us") to support business decisions regarding whether an alternative will be considered acceptable. Investing millions of dollars in the development and commercialization of an alternative is difficult to justify if there is uncertainty regarding which hazard endpoints and related toxicity tests are required to decide that the chemistry is "safe enough" or if there is a possibility that the chemical will be rejected by authorities or the scientific community as a regrettable substitute. Others acknowledged that data and information is ever evolving, and regulatory requirements may follow. Substitution decisions will need to utilize the best available data at any given time while ensuring sufficient data for the minimum requirements for making a safer determination.

Depending on whether an alternative is defined as a "new" versus "existing" chemical will dictate different regulatory requirements. Definitions of safety and acceptable use differ between regulatory paradigms in Europe under the Registration Evaluation and Authorization of Chemicals (REACH) regulation and in the U.S. under TSCA. California's Alternatives Analysis review process under its Safer Consumer Products regulation (regulations on 6PPD in tires are expected in 2023) will not decide as to whether an alternative chemical is safer; the regulatory review process is only focused on approving or disapproving the alternatives analysis report that is submitted by the priority chemicals' users and producers. Therefore, in this case, responsible entities (i.e., manufacturers) not regulators will provide a draft definition on toxicological criteria for safer. It is critical to engage communities (i.e., Tribal Governments, overburdened communities, etc.) that are impacted by 6PPD-quinone to identify solutions that restore the environment to a state that honors the importance of Washington's biota and people.

4. NEAR-TERM NEEDS TO IDENTIFY, EVALUATE AND ADOPT SUBSTITUTES FOR 6PPD IN TIRES

Substitution and the role of collaborative innovation processes

Joel Tickner, UMass Lowell

At the start of this session, participants heard about collaborations that came together for the replacement of various hazardous chemicals in specific applications. The key themes uniting these collaborations was the pressure to act (either regulatory or market), the significant and costly research needs that could be shared, the pre-competitive space of the incumbent hazardous chemical, as well as an independent entity to manage the project. These efforts were sometimes executed with companies and an NGO but could also include governments or universities. Three examples provided demonstrated the breath of possible collaboration mechanisms (e.g., an innovation challenge or a long-term consortium). The presentation ended with notes of caution about lessons learned. Collaborations must have clear performance and human and environmental safety criteria and commercialization should be de-risked once a safer alternative is identified, such as the use of financial incentives to offset some of the costs for the manufacturer or adopter of the alternatives.

Small Group Discussions – Barriers Constraining Substitution of 6PPD in Tires in the Near-Term

Forum participants worked in small groups to identify and discuss primary barriers constraining the identification, assessment, and adoption of antidegradant alternatives in the near-term. The definition of near-term was considered ~5 years.

Although there was broad agreement on the need for alternatives to 6PPD, participants cautioned that rushing towards near-term innovation solutions may be problematic given significant concerns about regrettable options both from a toxicity and performance perspective. There is a lack of historical health and environmental safety data for other alternative antidegradants, thus making a fast substitution risky. In addition, there are no accepted nor reliable accelerated tests for tire aging to substitute for field testing; moving faster than actual field tests support was also considered risky.

Participants identified a range of additional barriers constraining the identification of alternatives to 6PPD in the near-term, including those related to research, market penetration, and regulatory uncertainty.

Research Barriers:

- **Addressing the multi-functionality of 6PPD in tires.** As highlighted in formative presentations, 6PPD provides multiple antidegradant functions in tires, including protection against degradation of the rubber by ozone, oxygen, mechanical stress, and heat. Although different chemical alternatives may be able to provide the totality of these functions, using multiple rather than a single alternative complicates the innovation challenge given chemical-material compatibility needs. Those outside the supply chain of tires and rubber are at a disadvantage as they try to analyze the safety of potential alternatives to 6PPD because they may not be aware that certain multifunctional chemical combinations have already been discounted by industry due to their incompatibility with other rubber chemicals.

- **Inaccuracies related to 6PPD environmental transformation products.** One of the primary functions of 6PPD is to react with ozone to protect the rubber. However, this reaction transforms the chemical into the highly toxic 6PPD-quinione. Participants stressed the need for additional research on environmental transformation products of 6PPD and potential substitute PPDs because historical models in the literature do not accurately predict the quinone formation as a primary transformation product. Understanding the chemical mechanism of the quinone formation (and other possible toxic transformation products) could identify avenues for rational design (see below) that allow for the use of a substituted PPD, but without the toxic impacts.

- **Lack of knowledge regarding the mass-balance of 6PPD in tires and a lack of understanding of 6PPD distribution in tires and resulting releases into the environment.** A lack of understanding remains as to the levels of 6PPD and 6PPD-quinone being released into the environment from the tire itself (e.g., coming off the sidewall or the tread through tire wear particles). This information is necessary to inform whether a strategy that focuses on reducing 6PPD in specific components of the tire versus complete elimination will result in a satisfactory solution. Such data also informs the tire type that should be prioritized for 6PPD substitution, such as passenger vehicles or heavy commercial truck tires. Industry stakeholders stated that a near-term focus on the high-volume passenger tires is necessary because of the relatively higher complexity involved in changing heavy duty commercial truck tires or ones for military uses which have higher performance standards. Once success is shown in passenger tires, it becomes easier to integrate into other tires with higher qualification requirements.

- **Lack of a standardized "control" tire rubber formulation.** Since tire composition can widely vary, there is a need to develop a standardized control rubber formulation to support and align methods across different research groups engaged in assessing alternatives. Although alternative antidegradants will need to be tested in the variety of rubber formulations used, employing an agreed-upon control formulation was viewed as necessary to better focus and standardize research and innovation efforts on the topic.

- **The need for a clear impactful near-term goal to advance solutions-oriented research related to alternatives.** Although participants acknowledged that research is necessary, they recommended setting a clear and time-limited near-term goal that drives collaborative impactful research and funding towards solutions. Some participants were leery of simple calls for "more research" given that this is a repeatedly used strategy to delay preventative actions to mitigate harms associated with the use of toxic chemicals.

Market Barriers:

- **Lack of criteria for what is considered a toxicologically safer alternative to 6PPD in tires.** Participants stressed the need for specific criteria to guide toxicological evaluations of alternatives to 6PPD in tires as there is remains a lack of clarity regarding standards used for regulatory approvals as well as market/stakeholder expectations. Clear toxicological criteria also create product design parameters that are common to all researchers involved in the innovation or evaluation of alternatives.

- **Scaling alternatives in the volumes needed will be challenging.** A key barrier to bringing an alternative to 6PPD to the market is achieving widespread availability and scale, given that the antidegradant is used throughout the global tire industry in high volumes. It will be difficult for a single chemical supplier to produce a new antidegradant for tires at the scale currently needed; the involvement of multiple suppliers will be required. Tire manufacturers also prefer multiple suppliers to mitigate the risk of supply chain disruptions on tire production. Time frames and capital expenditures associated with changes in, or the establishment of new chemical manufacturing infrastructure will need to be financed as well. Participants also noted additional financial barriers including regulatory review costs especially if the chemical is new to the market.

- **Lack of collaborations working on 6PPD alternatives.** Participants indicated that a variety of collaborative structures were already present in the tire industry – such as the Tire Industry Program (TIP) of the World Business Council for Sustainable Development and CenTiRe. However, none of these groups have currently prioritized finding an alternative to 6PPD – there is a lack of sufficient financial support for alternatives development research. Joint development agreements are common legal tools to support collaborative R&D activities. However, these agreements have not been commonly used to support industry-wide collaborative chemical innovation in the tire industry.

Regulatory Barriers:

- **Concern for regulatory "goal posts" moving.** Concern that chemical management regulatory standards or "the goal posts" will shift over time were identified as a primary barrier to the innovation process. This concern included differences in national and state regulatory paradigms and uncertainty regarding how regulations will address emerging contaminants of concern, such as tire particles, microplastics and other sustainability issues related to tires.

- **Anti-trust considerations.** Some participants raised concerns that anti-trust laws may be barriers to collaborative research and innovation processes. Ground rules and adherence with relevant anti-trust laws need to be established as part of pre-competitive research collaborations. Based on the experience of participants in the room, there are procedural ways to address anti-trust considerations, such as ensuring that the activities of participants are neither involved in fixing prices, inhibiting competition, nor pushing specific competitors out of the market. Research alone is rarely an anti-trust consideration.

Small Group Discussions – Near-Term Opportunities for 6PPD Alternative Development and Implementation

Despite the barriers outlined above, participants identified a range of opportunities to advance research, trust, transparency, and cost-sharing to advance work on alternatives to 6PPD in tires in the near-term. The discussions demonstrated that competitors are willing to work together to solve common challenges.

Research Opportunities:

- **Conducting rational design research.** Group discussions highlighted the potential opportunity of using rational design techniques to modify the parent compound of 6PPD or another PPD. The goal of a rational design approach is to identify regions on the 6PPD molecule or another PPD that could be modified to negate the quinone formation as well as lessening the inherent toxicity impacts related to reproductive toxicity and acute aquatic toxicity while preserving the antidegradant functionality. There are successful models utilizing this approach, for example Valspar's alternative to bisphenol-A in can linings that identified a bisphenol that had the functional performance needed but did not demonstrate endocrine disrupting effects.[24] In addition, tools such as those through U.S. EPA's CompTox program[25] can be of assistance. Other industries' antioxidants and antiozonants could also be a source of potential rationale design candidates.

- **Understanding 6PPD-quinone formation and 6PPD releases into the environment.** Participants generally agreed that two questions still need to be answered in relation to 6PPD. However, filling these research gaps should not delay research on alternatives. First, what environmental factors impact the quinone formation on 6PPD and other PPDs? Such molecular understanding would help inform rational design models for alternatives. Second, what is the concentration of 6PPD that is released into the environment by different tire types and tire components (sidewall or tread)? This information is needed to better target substitution efforts that will impactfully mitigate 6PPD-quinone concentrations in vulnerable watersheds.

- **Using less 6PPD or contain its release to the environment?** One near-term option mentioned was whether less 6PPD could be used or whether coatings could be developed to stop its release to the environment. This option only focuses on the use phase of tires and would not address 6PPD emissions during production or end of life/recycling.

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[24] See more about Valspar's alternative development here.
[25] See more about EPA's CompTox program here.

Collaborative Structures:

- **Developing a definition of safer for a 6PPD alternative.** There was an explicit call to advance a consistent understanding of the requirements needed to determine whether the toxicity of an alternative is safer than 6PPD. Such requirements should include clear criteria and appropriate test methods as needed. Participants did not reach a consensus regarding the method by which to determine this definition, as it could be achieved through a collaborative or regulatory structure.

- **Establishing an alternatives development roadmap for 6PPD in tires.** Such a roadmap is important as it helps to create a path towards the innovation goals, establish critical standards related to toxicity assessments and chemical/product performance, capital needs, etc. A roadmap also provides clarity for executives within chemical suppliers and tire manufacturers regarding the business case for innovation and required resource needs. Industry participants were particularly interested in outlining which toxicological tests or tools to employ at specific research and development stages of the antidegradant, from basic research to product demonstration research stages.

- **Establishing a collective agreement and timeline for phasing out 6PPD in tires.** Some Forum participants noted that an industry-wide agreement and associated timeline for phasing out 6PPD in tires could be a critical enabler for innovation efforts. Such an agreement could provide greater certainty for the value chain and help to drive government and private sector investment in the research and innovation process. Some participants suggested that regulatory actions, such as a restriction on 6PPD in tires, could provide such timelines. Nonetheless, the use of voluntary agreements by the industry outside of regulatory requirements would advance progress.

- **Developing a 3rd party toxicology review committee.** Given the need for increased toxicology expertise in many smaller chemical suppliers as well as within the tire industry, there was a recommendation to establish a third-party toxicology review committee to support the preliminary screening of alternatives identified based on their inherent hazards and environmental fate properties. The purpose of such an entity would be to simply identify potential red flags that could screen out potential alternatives quickly to keep the innovation process moving forward on toxicologically safer alternatives.

- **Creating a pre-competitive data repository on alternatives.** Such a repository could be modelled after similar collaborations in other sectors, such as the Pistoia Alliance,[26] which was established in 2007 to lower barriers to collaboration and innovation among major actors in the pharmaceutical industry. Through the Pistoia Alliance, volumes of basic data (e.g., solubility data, viscosity data) have been shared to support drug discovery efforts by member companies. In the case of tires, basic

[26] See more about the Pistoia Alliance here. Accessed January 2023.

data on engineering performance and toxicological properties could be a focus. Often knowledge about the physicochemical properties of chemicals that are not selected for a given function is just as important as the preferred chemicals. Having a comprehensive data library is a critical asset for innovation and important to support the sharing of information on failed alternatives so that researchers do not spend their time on such alternatives. This information could also be used to avoid targeted toxicity tests of chemicals that were not deemed viable by the industry. Some participants also noted that under the California Safer Consumer Products Program, the Department of Toxic Substances Control is expected to require tire manufacturers to conduct an alternatives analysis on 6PPD in tires (*note, this is currently in a proposal stage*).[27] This alternatives analysis is expected to compile existing data on potential alternatives that will be made publicly available and of value to future research efforts.

Funding Mechanisms:

- **Incentivizing multi-disciplinary research teams.** Participants encouraged funding programs to support the formation of research partnerships that are inclusive of the expertise needed to discover safer and effective alternatives to 6PPD in tires. Chemical, engineering, and toxicological expertise is needed in these research teams.

- **Supporting industry-academia research.** Some participants emphasized the need for government entities to support and drive the research needed. Participants suggested using existing as well as developing new industry-academic collaborative research models. CenTiRe (an Industry-University Cooperative Research Center (IUCRC) supported by the National Science Foundation (NSF) and tire industry members)[28] is one such existing model. However, no academic public health experts are currently affiliated with CenTiRe, but this could change. Some participants cautioned that the support available through IUCRC programs typically is only enough to fund a doctoral student or two and is not the type or level of funding needed for the current innovation challenge.

- **Supporting research by the tire industry.** There was a call for the tire industry to sponsor research on alternatives. The Pistoia Alliance is one model for how the tire industry could directly support external pre-competitive research competitions.

Other Near-Term Opportunities:

- Although the topic of mitigation was not the focus of this meeting, participants raised the need for and investment in mitigation strategies (both research and deployment of identified technologies) as antidegradant alternatives are being developed.

[27] California Department of Toxic Substance Control. Safer Consumer Products Program. Proposed Priority Product: Motor Vehicle Tires Containing 6PPD Accessed January 2023.
[28] See more about CenTiRe here. Accessed January 2023.

5. LONG-TERM NEEDS TO IDENTIFY, EVALUATE AND ADOPT SUBSTITUTES FOR 6PPD IN TIRES

Meeting participants wrestled with the needs for replacing 6PPD in tires within the context of future product development trends confronting the tire and transportation industry in the next 10-15 years. There are a range of additional tire design innovation needs confronting the industry, such as:

- **Moving toward electric vehicles.** The batteries in electric vehicles create more weight and more torque in the automobile and thus more load on the tires. An increased load means greater tire wear. The need for antidegradants will therefore likely increase with the transition to electric vehicles to maximize their product life.

- **Reducing CO_2 emissions broadly**. Companies are increasingly committing to greenhouse gas emission reductions throughout the entire life cycle of their products. A new antidegradant should not increase greenhouse gas emissions, particularly Scope 3 emissions (which refer to the emissions of CO_2 from a product that a company is indirectly responsible for upstream and downstream of production).

- **Growing commitments to use more sustainable domestic natural rubber sources**. Natural rubber generally needs more degradation protection than synthetic rubber. There were suggestions that higher amounts of an antidegradant may be needed if the proportion of natural rubber increases in the tire due to its sustainability benefit.

- **Growing concerns about tire particles and waste.** Any alternative antidegradant should strive to maintain or extend the lifetime of the tire. In addition, the antidegradant should not inhibit waste tire use (such as in turf fields) or increase the toxicity of ubiquitous tire wear particles.

- **Growing focus on the development and deployment of non-pneumatic tires**. These "air-less" tires do not have a sidewall, which is a source of 6PPD in tires. There is still a need for antidegradants in the surface tread, but overall non-pneumatic tires may use much less mass of antidegradants than current tire designs. These tire designs are not currently approved for use by NHTSA.

Through a plenary discussion, participants talked about balancing near-term versus long-term needs considering how other innovation factors facing the tire industry might impact the development and use of alternative antidegradants. Themes included:

- **Certain components of tires routinely change, but not all.** There is always innovation happening related to the treads of tires driven in part by the auto manufacturers' desire for improved ride and handling, grip and rolling resistance, and other factors. Changes to the design of treads for truck tire are not as common and more involved than for passenger tires. Some participants raised concern regarding the inherent difficulty in changing a tire's internal components, especially the rubber coating on the steel belts. This component rarely changes (**see 1st and 2nd Belts in FIGURE 3**) because its performance is essential to the function of the tire and is where catastrophic events could occur. 6PPD is added in the formulation of all tire components, with the exception to the thin inner liner. Components of the tire that are areas of continued optimization, such as the tread and sidewall, could be an earlier opportunity for changes in the antidegradant(s) used, compared to tire components that change less frequently. However, 6PPD is mobile in the tire and can migrate from its original location to the tire surface throughout the tire lifetime.

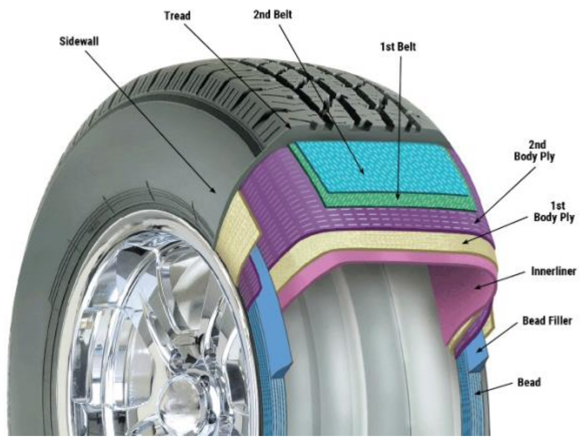

FIGURE 3: Tire components, which include components made in part with metals (bead and belts), fibers (body ply) and rubber (tread, sidewall, inner liner, etc.).
Source: US Tire Manufacturers Association[29]

- **Tension between incremental versus a "final solution".** Given the capital investment needed to change production (whether chemical or tire), it is not desirable to undertake one change in the near-term and a more optimal change in the long-term, unless that change is essentially a "drop-in". These concerns were raised in response to the question as to whether shifting to a non-ideal alternative (e.g., another PPD that has less impacts, but not optimized against all toxicological criteria) could occur while still researching and investing in a longer-term solution. However, some meeting participants also stressed that incremental improvements are often how change is made throughout both the tire and chemical industries; the natural course of progress are improvements that build on each other while recognizing that tire safety cannot be comprised.

6. MOVING FORWARD AND NEXT STEPS

There was a clear commitment from Forum participants to work collaboratively to drive solutions that address the impacts being caused by using 6PPD in tires. The Forum itself helped to enhance understanding and trust across the multiple stakeholder groups in

[29] USTMA What's in a tire? Accessed January 2023.

attendance, which is foundational to the viability of future collaborative efforts. At the close of the Forum there was a call to continue the effective dialog that began at the event and an expressed interest in collaborating in a pre-competitive environment to accelerate the pace of innovation of alternatives to 6PPD. Important next steps outlined include:

- **Define "safer" minimum toxicological criteria for alternatives to 6PPD to support the research and innovation processes.** This was a critical next step identified by Forum participants. There was a recommendation to use existing criteria for defining safer alternatives, such as Washington's Criteria for Safer,[30] as a starting point. Criteria need to address the issue of environmental transformation products and provide guidance regarding required test species for evaluating aquatic toxicity, including what evidence is sufficient to indicate that the toxicity of an alternative chemical is safer than 6PPD.

- **Fund pre-competitive multidisciplinary research to advance effective and safer alternatives to 6PPD.** The initial focus of research suggested by participants include:
    - Understanding 6PPD-quinone release from various components of the tire to improve predictive monitoring.
    - Integrating quinone transformations into rational design frameworks to reduce regrettable substitutions.
    - Integrating toxicity considerations into the antidegradant innovation pipeline to "fail faster," reducing investments in unsuccessful innovations.

  Developing solutions in the form of 6PPD alternatives should be the focus of research efforts. There was broad agreement that research teams involved in developing 6PPD alternatives should reach beyond material scientists, chemists, and chemical engineers to also include toxicologists, environmental engineers, and health scientists. A range of funding sources could be tapped to provide the support needed, including targeted funding from federal and state research programs, industry-supported research programs, and industry-academic research partnerships, among others.

- **Develop and advance specific collaborations to scale the pace of innovation.** Forum participants identified several specific collaboration ideas such as information-sharing tools, third party toxicity evaluation, and collaborative chemical safety and chemical performance testing programs. However, additional work by the chemical and tire industries is needed to focus and outline desired collaborative approaches, including goals, potential partners, coordination roles.

[30] Washington State Department of Ecology. Regulatory Determinations Report to the Legislature: Safer Products for Washington Cycle 1 Implementation Phase 3. June 2022.

- **Explore establishing a voluntary commitment to phase out the use of 6PPD in tires by tire manufacturers, as a regulatory restriction has not been enacted**. Some stakeholders proposed that an explicit substitution goal and timeline would help increase and direct investment and capacity in the research and innovation processes on alternatives to 6PPD. The tire industry and chemical sector would have increased certainty and confidence in the industry-wide innovation need. Such a commitment would need to be guided by a clear roadmap for innovation, commercialization, and adoption of alternatives to 6PPD that outlines research, investment, and collaboration needs.

Replacing 6PPD in tires is a complex innovation challenge that requires balancing and optimizing performance, human and environmental health, and sustainability attributes. Participants walked away from the Forum understanding the challenges ahead but also generally recognizing a shared concern and the clear need for decisive action given the growing evidence of impact on a species of significant cultural, community, and economic value. The question discussed by participants was not one of whether 6PPD should be replaced but rather how to get there. Participants discussed the information, collaborations, and resources that will be needed to accelerate the pace of development, commercialization, and adoption of innovations that minimize impact to ecosystem and human health - while not compromising tire performance and passenger safety. Participants noted that building stronger and common understandings of goals, research needs, criteria, and measures of success can help guide resources and expedite actions to address the 6PPD challenge. The positive, open, and engaged discussions and feedback from the Forum provide evidence that the "collaborative innovation"[31] approach can play an important role in addressing current and future chemical challenges in a pre-competitive space where pressures to act are elevated.

[31] Becker M, Tickner JA. Sustainable Chemistry and Pharmacy. 2020;18:100330. https://doi.org/10.1016/j.scp.2020.100330

APPENDIX

A. Participating Organizations

Academia	University of Massachusetts Lowell
	University of Akron
	University of California Berkeley
	University of Washington
	Washington State University
Tire Manufacturers and their Associations	Bridgestone Americas Inc.
	Continental Tire
	Goodyear Tire & Rubber Company
	Michelin
	United States Tire Manufacturer's Association
Chemical Suppliers	Flexsys
	SI Group
	Silpara Technologies LLC
	Thomas Swan / Swan Chemical
Consultants	DK Enterprises
	Gradient
	Hunton Andrews Kurth
	Polymer Technology Services LLC
	ToxStrategies
NGOs	ChemFORWARD
	Columbia River Inter-Tribal Fish Commission
	Green Chemistry & Commerce Council
	Tire Industry Project, WBCSD
	Toxics Free Future
Performance Labs	ACE Laboratories
	Smithers
Government Agencies	California Department of Toxic Substances and Control
	Environment and Climate Change Canada
	U.S. Department of Agriculture
	U.S. Department of Defense, Strategic Environmental Research and Development Program (via Noblis)
	U.S. Environmental Protection Agency
	U.S. Geological Survey
	Washington State Department of Ecology

B. Forum Agenda

8:00 AM	*NAME BADGE PICK-UP: LIGHT BREAKFAST PROVIDED*
8:30 AM – 8:45 AM	**Welcome Remarks**
8:45 AM – 9:45 AM	**Setting the Context: Thinking About Alternative Antidegradants for Tires** **6PPD: the problem** Edward Kolodziej, University of Washington **A tire industry perspective on 6PPD replacement: the challenge** Chris Robertson, Polymer Technology Services LLC **What do we know about the alternatives?** Aude Bechu, UMass Lowell Miles Dearth, ACE Laboratories **How to think about substitution** Joel Tickner, UMass Lowell
9:45 AM – 10:00 AM	*15-MIN BREAK*
10:00 AM – 12:15 PM 10:00 AM – 10:30 AM 10:30 AM – 11:30 AM 11:30 AM – 12:30 PM	**Exploring Critical Design Considerations. What is Safe Enough? What is Sufficient Performance?** ***Formative Presentations*** **Current practices for making a "safer" determination** Molly Jacobs, UMass Lowell **Performance requirements for antidegradants in tires** **Laboratory Scale** - Erick Sharp, ACE Laboratories **Product Scale** - Bruce Lambillotte, Smithers o Reflections from Jamie, McNutt USTMA ***Small Group Work*** **Group SAFER:** What are critical endpoints for making a safer determination for an alternative to 6PPD in tires? How should transformations products be considered? What methods/tools could be used? Who needs to be involved? **Group SUFFICIENT PERFORMANCE:** What should be considered for understanding the functional performance needs of alternatives to 6PPD in tires? What are critical performance requirements and related performance tests and standards for acceptable performance? Who needs to be involved? ***Report Back and Discussion***
12:30 PM – 1:30 PM	*LUNCH*
1:30 PM – 2:45 PM 1:30 PM – 1:40 PM 1:40 PM – 2:40 PM 2:40 PM – 3:00 PM	**Near-Term Needs to Identify, Evaluate and Adopt Substitutes for 6PPD in Tires** ***Formative Presentation*** **Substitution and the role of collaborative innovation processes** Joel Tickner, UMass Lowell ***Small Group Work*** Considering use of the "Safer" and "Sufficient Performance" considerations, what are the R&I needs and collaborative opportunities to replace 6PPD with safer and effective substitutes in the **near term**? Any additional adaptations to design considerations given near-term needs/opportunities? ***Report Back and Discussion***
3:00 PM – 3:15 PM	*15-MIN BREAK*
3:15 PM – 4:15 PM	**Long-Term Needs to Identify, Evaluate and Adopt Substitutes for 6PPD in Tires** ***Plenary Discussion*** Considering use of the "Safer" and "Sufficient Performance" considerations, what is needed to rethink innovation regarding the role of antidegradants in tires that can result in fundamentally safer options for the **next generation-design** of tires (15+ years), including new product designs AND new sustainable chemistry options?
4:15 PM – 5:00 PM **5:00 PM**	**Moving Forward and Next Steps** **Closing**

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Sustainable Chemistry Catalyst

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