



October 8, 2021

Ken Zarker, Craig Manahan
State of Washington
Department of Ecology
P.O. Box 47600
Olympia, WA 98504-7600

Re: Department of Ecology research on 6PPD and proposed alternatives to 6PPD

Dear Ken and Craig,

This letter is intended to provide the State of Washington Department of Ecology with additional information about the technical feasibility of several antioxidants and antiozonants currently being evaluated by the Department. We understand that the Department is currently conducting research in response to Washington Senate bill 5092 which provides \$195,000 to the Department to “assess potential hazards of 6PPD (CAS 793-24-8) and other chemicals or chemical classes and breakdown products used as antioxidants and/or antiozonants in tires and submit a technical memo to the appropriate committees of the legislature by December 1, 2021.”

We thank the Department for sharing the list antioxidants and antiozonants that will be assessed for their potential hazards. Alternatives to 6PPD must provide the same functions as 6PPD in a tire to ensure tire safety and performance. Several of the substances that are being assessed by the Department do not meet the needed functions to be considered as possible alternatives to 6PPD. Other substances that are being assessed by the Department lack enough information at this time to be considered as an alternative to 6PPD. Below is an overview of each of the antioxidants and antiozonants being assessed by the Department and additional information about whether these substances provide the needed functions to be considered an alternative to 6PPD.

USTMA and our members are committed to supporting an alternatives analysis of 6PPD in tires under the California Department of Toxic Substances Control (DTSC), Safer Consumer Products Regulations (SCPR). We encourage continued coordination and collaboration of the Department and DTSC on the alternatives analysis for 6PPD in tires under the SCPR.

I. Overview of the functions 6PPD provides in manufacturing safe and durable tires

6PPD is the most effective antioxidant and antiozonant and is utilized by all USTMA members. 6PPD reacts rapidly with ozone and can last the lifetime of a tire. The reason it can last until an 80,000-mile tire is worn out is that only part of it dissolves in the rubber when it is mixed into the rubber compound. The antiozonant migrates through the rubber to the surface during the operation of the tire where it forms a film. The film reacts with ozone, and as it is used up, more antiozonant moves to the surface. The dispersed but undissolved 6PPD in the rubber compound eventually dissolves as 6PPD is depleted (used up) and serves as a reservoir during the lifetime of the tire. If the migration of the

antiozonant is too slow, the tire will not be fully protected; if the migration rate is too fast, the antiozonant will be used up before the tire is worn out. It should also be noted that the oxidation products from 6PPD are also effective antioxidants/antiozonants although not as effective as 6PPD. This also contributes to the ozone protection provided during the life of the tire.

6PPD is also an antifatigue agent. Antifatigue agents reduce the degradation of the rubber compound that takes place during the flexing of the tire. Flexing builds heat, which causes degradation. Underinflated tires cause excessive flexing and high heat buildup, which can lead to unsafe conditions. In 2014 it was reported that 7 out of every 10 vehicles had at least one underinflated tire.¹ In addition to providing protection against ozone, 6PPD will also greatly reduce the rate of reaction of the rubber with oxygen in the atmosphere.

Thus, alternatives to 6PPD must also meet these critical functions and have the following qualities:

- Continuously present at the surface of the tire to ensure protection of the rubber compound from degradation due to oxygen and ozone;
- Adequate solubility and diffusivity in rubber compounds;
- Reactive with ozone but not too reactive in order to prevent premature depletion;
- No adverse effects on the rubber processing;
- Available in rubber compound over a tire's entire life cycle to ensure protection of the rubber;
- Low toxicity of the material and any transformation products; and
- No adverse effects on tire safety and performance.

II. Antioxidants and antiozonants that are being evaluated by the Department of Ecology

A. Substances that do not provide the critical functions necessary to be considered an alternative to 6PPD

1. CCPD, CAS number 4175-38-6

CCPD is also a member of the PPD class of chemicals. Thus, this material may have the potential to form a quinone and it is unknown if other PPD substances cause the same impact on coho salmon. CCPD is not considered a safer alternative to 6PPD as this material would not be expected to provide the lasting protection needed to protect the rubber compound through a tire's useful life. This material is similar to 77PD in that it migrates through the rubber faster than 6PPD and is expected to only provide 1-2 years of protection from oxygen and ozone.

2. IPPD, CAS number 101-72-4

IPPD is also a member of the PPD class of chemicals. Of all of the chemicals in the PPD class, IPPD has been shown to show the highest level of skin sensitivity and therefore is not considered a safer alternative to 6PPD. As a member of the PPD family, this substance also has the potential to form quinone and it is unknown if other PPD substances cause the same impact on coho salmon.

¹ <https://www.tirereview.com/rma-70-vehicles-underinflated-tires/>

3. TMQ 26780-96-1

This is used in tire compounds today as a co-antiozonant/antioxidant with 6PPD. By itself, it has been shown to have only 52% of the activity of 6PPD. By itself, it does not provide sufficient antiozonant protection to the rubber.

4. 6QDI 52870-46-9

This is an oxidation product of 6PPD and has the same carbon framework. It has been shown to be both an effective antiozonant and antioxidant, but its chemistry on aging produces 6PPD, and thus the 6PPD quinone would be produced from tires containing this material.

5. NBC 13927-77-0

This compound would be expected to act as an antiozonant, but would render the compound very difficult if not impossible to process in a tire plant. Additionally, it contains the heavy metal nickel. Some of the warnings listed include the following:

- May cause an allergic skin reaction [Warning Sensitization, Skin]
- Causes serious eye irritation
- May cause allergy or asthma symptoms or breathing difficulties if inhaled
- Suspected of causing cancer [Warning Carcinogenicity]
- May cause long lasting harmful effects to aquatic life

6. Dilauryl thiodipropionate 123-28-4

This compound is used as an antioxidant to protect synthetic polymers made in a chemical plant until they are used in a tire plant. It is expected to have little, if any antiozonant activity.

B. Substances where there is not enough information to be considered an alternative to 6PPD

1. 77PD, CAS number 3081-14-9

77PD is a member of the PPD class of chemicals. 77PD does not meet the critical functions needed to be a safer alternative to 6PPD as 77PDA migrates through rubber faster than 6PPD and thus it provides a shorter period of protection than 6PPD. Research conducted in the 1950's demonstrates that the use of this material in combination with other stabilizers in high ozone areas was shown to have effective protection against oxygen and ozone for only 1-2 years.² It is unclear how long the protection would last in a modern tire. It may be possible to combine this material with other members of the PPD family for longer tire life, but this would take extensive tire testing and research. Equally important is the fact that as a member of the PPD family, it would be expected to form a quinone like 6PPD. To date, it is unknown if other chemicals in the PPD family will form a quinone and whether they would cause the same impact on coho salmon.

² "Weather aging of elastomers on military vehicles" W. England, J. Krimian and R. Heinrich, Rubber Chemistry and Technology, (1959) 32 (4): 1143-1154.

2. 7PPD 3081-01-4

7PPD is a member of the PPD class of chemicals and is extremely similar to 6PPD in chemical structure. There is only a one carbon difference in the two structures. It would be expected to be an excellent antiozonant, an excellent antioxidant, an excellent antifatigue agent, migrate at approximately the same rate as 6PPD, but also form a quinone very similar to 6PPD.

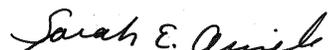
3. Ethoxyquin 91-53-2

This compound was an early candidate for tires in the 1950's and was used in some tires during that period. In early studies, it was shown to be 87% as effective as 6PPD in the initial reaction with ozone. The migration rate is not known, so it is unclear how long protection would last. It is classified as mildly to moderately toxic. The by-products of ozonation have not been fully characterized, and their toxicity is unknown.

III. USTMA welcomes the opportunity for continued engagement with the Department on the assessment of potential hazards of 6PPD and other antioxidants and antiozonants

USTMA thanks the Department for their continued engagement with USTMA on this important issue. We recognize the importance of filling relevant data gaps on 6PPD-quinone as expeditiously as possible. We look forward to meeting on October 12th with the Department and researchers from the University of Washington and the Washington Stormwater Center to review relevant data gaps and to discuss efforts underway to fill critical data gaps.

Thank you again,



Sarah E. Amick
Vice President EHS&S and Senior Counsel
U.S. Tire Manufacturers Association