Preliminary Alternatives Analysis Report:
N-1,3-dimethyl-butyl-N'-phenyl-p-phenylenediamine
(6PPD) found in treads

Prepared by:

Borrachas Vipal S.A.

March 28, 2024

TABLE OF CONTENTS

EXECUTIVE SUMMARY 3
1.0 PREPARER INFORMATION 4
2.0 RESPONSIBLE ENTITY AND SUPPLY CHAIN INFORMATION 6
3.0 PRIORITY PRODUCT INFORMATION 7
3.1 Priority Product Function 8
3.2 Priority Product Performance 8
3.3 Priority Product Legal Requirements 9
3.4 Role of the Chemical(s) of Concern 9
3.5 Is the Chemical(s) of Concern or Alternative Replacement Chemical(s) necessary? 9
4.1 Relevant Factors 10
4.2 Exposure Paths 11
4.2.1 Chemical Quantity 11
4.2.2 Exposure Factors 11
4.3 Consideration of Additional Information 12
5.0 SCOPE AND COMPARISON OF ALTERNATIVES 14
5.1 Alternatives Considered 14
5.2 Rationale for Alternatives not Selected 14
5.3 Comparison of Chemical(s) of Concern and Alternative Replacement Chemical(s) 15
6.0 SELECTED ALTERNATIVE(S) 22
7.0 WORK PLAN 22
7.1 Discussion of Proposed Tasks to Generate the Final AA Report 22
7.2 Proposed Implementation Schedule 23
REFERENCES 24

EXECUTIVE SUMMARY

The Department of Toxic Substances Control (DTSC) identifies combinations of chemicals considered priority products according to the process identified in Article 3 of the Safer Consumer Products Regulations (SCP). DTSC has determined that motor vehicle tires containing N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) must meet key prioritization criteria. To comply with this regulation, the company Vipal, one of the largest manufacturers of rubber products worldwide, always aims to improve its products to offer its customers the most advanced technologies. Therefore, all necessary actions foreseen in the new regulation agenda are already being handled and prepared internally. Considering that the path to innovation is constantly evolving, the team of experts has been conducting research focused on the scope of this regulation since 2014. Confident the products will meet the required regulatory requirements, delivering total security and reliability to customers and reaffirming the commitment to quality, we aim to comply with all regulations. The company is in the study phase to reduce percentages of 6PPD, and to seek alternative options to completely eliminate 6PPD from its products, according to the work plan presented in item 7.0.

1.0 PREPARER INFORMATION

Preparer Information:

First Name	**Daiane**
Last Name	**Torani**
Job Title	**R&D analyst**
Company	**Borrachas Vipal S.A.**
Email	**daiane.torani@vipal.com.br**
Phone	**+555432423800**
Address	**Italia Street, 787 Zip Code: 95320-000 City: Nova Prata/RS - Brazil**

Responsible Entities Information:

First Name	**Janaína**
Last Name	**Silva Crespo**
Company	**UCS**
Business Type	**researcher**
Email	**Janaina da Silva Crespo <jscrespo@ucs.br>**
Phone	**54 3218-2100**
Website	**www.ucs.br**
Address	**Francisco Getúlio Vargas street, 1130 – Zip Code 95070-560 City: Caxias do Sul/ RS - Brazil**

First Name	**Jordão**
Last Name	**Gheller**
Company	**SENAI Institute of Innovation in Polymer Engineering**
Business Type	**researcher**
Email	**genilson.pacheco@senairs.org.br**
Phone	**(51) 3904-2700**
Website	**www.senairs.org.br/institutos/engenharia-de-polimeros**
Address	**Pres. João Goulart Ave., 682, Zip Code: 93030-090 City: São Leopoldo/RS - Brazil**

CERTIFICATION AND SIGNATURES

“I certify that this document and all attachments were prepared or compiled under my direction or supervision to assure that qualified personnel properly gathered and evaluated the information submitted. Based on my inquiry of the person(s) directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I understand that submitting false information or statements is a violation of the law.”

Responsible Entity Signature: Rodemir Conte

Date: March 28, 2024

2.0 RESPONSIBLE ENTITY AND SUPPLY CHAIN INFORMATION

Manufacturer(s) and Importer(s):

Below are the contact details of the suppliers or manufacturers of the materials to be tested. This list should not be considered definitive, as new alternatives may emerge as the study develops.

First Name	**Fernando**
Last Name	**Lagni Martins**
Company	**Flexys**
Business Type	**Manufacturer**
Email	**Fernando Lagni Martins <FernandoLagni.Martins@Flexsys.com>**
Phone	**55 11 99114-6488**
Website	**www.flexsys.com.br**
Address	**Barata Ribeiro street, 79 Zip Code: 13015-097 City: Campinas/SP - Brazil**

First Name	**Mariano**
Last Name	**Richter**
Company	**CYA**
Business Type	**Manufacturer**
Email	**mariano.richter@cya.com.br**
Phone	**+55 51 3452-3500**
Website	**www.cya.com.br**
Address	**Severo Dullius Ave., 1395 Zip Code: 90200-310 City: Porto Alegre/RS – Brazil**

First Name	**Alfredo**
Last Name	**Nunes**
Company	**LANXESS Ind. Prod. Químicos e Plásticos Ltda**
Business Type	**Manufacturer**
Email	**alfredo.nunes@lanxess.com**

Phone	**+55 11 3741.2986**
Website	**www.lanxess.com**
Address	**João Scarparo Netto Ave., 84 Zip Code: 13080-655 City: Campinas/SP - Brazil**

Manufacturer(s), Importer(s), and /or Distributor(s) listed on the Priority Product label:

Company	**Vipal Rubber Corporation**
Email	**info@vipal-usa.com**
Phone	**305 640 0330**
Website	**www.vipal.com**
Address	**2601NW 89 Court/Miami - FL, 33172 – United States**

Company	**Marangoni Tread North America**
Email	**info@mtna-us.com**
Phone	**615 868 4050**
Website	**www.mtna-us.com**
Address	**708 Myatt DR. Madison – TN, 37115 – United States**

For strategic business reasons, the list of customers will not be made available at this time.

3.0 PRIORITY PRODUCT INFORMATION

Brand name(s)	Vipal
Product name(s)	Borrachas Vipal S.A
Product description(s)	Retread material for tires
Chemical(s) of Concern	N(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

Brand name(s)	Vipal
Product name(s)	Borrachas Vipal S.A
Product description(s)	Motorcycle tires
Chemical(s) of Concern	N(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

Brand name(s)	PB Tread
Product name(s)	Borrachas Vipal S.A
Product description(s)	Retread material for tires
Chemical(s) of Concern	N(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

Brand name(s)	Ruzi
Product name(s)	Borrachas Vipal S.A
Product description(s)	Retread material for tires
Chemical(s) of Concern	N(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

Brand name(s)	Marangoni
Product name(s)	Marangoni Tread North America inc.
Product description(s)	Retread material for tires
Chemical(s) of Concern	N(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

3.1 Priority Product Function

Among the functional requirements of a tread are keeping the vehicle in contact with the ground, providing grip and resistance to wear, in addition to maintaining integrity throughout its useful life.

Among the functional requirements of a motorcycle tire are transforming engine power into driving force through adhesion to the ground, absorbing impacts, supporting load, ensuring the tire's drivability and performance through wear resistance.

3.2 Priority Product Performance

Among the performance requirements of a tread and a motorcycle tire are keeping it able to protect against the attack of external agents, such as ozone, oxidation and temperature, preserving the functional requirements of the product.

This protection must be preserved throughout the period of validity and/or use of the product.

3.3 Priority Product Legal Requirements

The legal requirements regarding treads are those assigned by the EPA's Smartway program, while those for motorcycle tires are those required by the NHTSA, according to the FMVSS regulation, Safety Standard No. 119.

3.4 Role of the Chemical(s) of Concern

It is currently known that most of the degradation found in elastomers is due to oxygen or ozone. Although the latter is only found in small quantities, the effects can be devastating, especially for rubbers in dynamic work. The outcome is the early cracks in the direction of stress. The rate of crack growth increases with tension and will be fast enough to render the rubber useless.

In spite of all the research carried out to improve the service life of rubber products, antidegradants should last longer in rubber compounds to provide long-term protection. Currently, commercial tires need better sidewall protection as they are increasingly retreaded.

6PPD has molar mass of 268 g/mol. It is a stabilizer with high compatibility with elastomers, presenting low volatility. 6PPD can provide excellent protection against degradative forces for all rubber vulcanizates.

It is widely used in different sectors of the rubber industry, as it offers excellent resistance to vulcanizates against degradation caused by ozone (static as well as dynamic), flexural cracking, thermo-oxidative aging, oxidative aging catalyzed by metal ions, ultraviolet rays and bad weather (RAPTA et.al., 2009). Para-phenylene diamines are considered stabilizers whose function is to break the chain (via the donation of a hydrogen atom) forming an aminyl radical (GUGUMUS, 1990). There are no known other antidegradants that fulfill the same function of delaying aging through dynamic work as 6PPD.

3.5 Is the Chemical(s) of Concern or Alternative Replacement Chemical(s) necessary?

Rubber compounds can be degraded by reactions with oxygen, ozone, light, metal ions and heat. Antidegradants protect rubber against aerobic aging (oxygen) and ozone attack. They are of prime importance and play a vital role in rubber products, keeping properties in serviceable condition.

It has been proven that para-phenylene diamines are good anti-fatigue agents and that diarylamine nitroxyl radicals are even more effective than the original amines. The antifatigue mechanism of amine antidegradants has been proposed where the formation of intermediate nitroxyl radicals plays an active role (DWEIK; SCOTT, 1984).

In the fatigue process, macroalkyl radicals are generated and subsequently removed by reaction with these nitroxyl radicals. The resulting hydroxylamine can be reoxidized by alkylperoxy radicals

that regenerate nitroxyl radicals in a process that breaks the autooxidation chain. The reaction of this antidegradant is important to stabilize degradation by the Fatigue mechanism.

According to the literature cited below, studies already carried out aimed at reducing and/or replacing 6PPD in elastomeric formulations for treads.

According to tests carried out by CARPENEDO *et al* (2020), proportions of 0, 0.5, 1.0, 1.5 and 2.5 of 6PPD were evaluated in elastomeric formulations applicable to tires. According to the results, it was not possible to reduce the 6PPD content due to the drop in mechanical properties after aging; such properties are important to provide safety when using the final product. According to the authors for the aforementioned application, the most appropriate concentration of stabilizing additives to maintain the mechanical properties of the compositions studied was 2.5 phr of 6PPD and 1.0 phr of TMQ. The use of higher TMQ contents did not contribute to the improvement of mechanical properties.

According to an assessment carried out by MAUSS, C. J. (2020), tire treads, as well as motorcycle tires, must have appropriate protective agents to prevent changes in properties due to deterioration of the elastomeric composition. In this work, eucalyptus lignin samples obtained by the kraft process (LIGK and LIGKF) were studied as a renewable alternative in tire tread formulation regarding their antioxidant performance in comparison to TMQ (non-renewable), alone (2 phr) or in conjunction with 6PPD (1.0, 1.5 or 2.0 phr). In general, lignins provided low protection against oxidation, similar or more effective than TMQ in the studied rubber composition (evaluations through accelerated thermal aging and OIT). No significant variations in processing, rheological, physical and mechanical properties were observed in the compositions. It was found that using 6PPD as an ozone protection agent is necessary as the tread is exposed to ozone. Among the protective combinations evaluated in this work, TMQ and lignin did not show effective resistance to ozone. However, in combination with 6PPD, unlike TMQ which exerts a synergistic effect on ozone resistance, lignin samples negatively interfered with the action of 6PPD.

Vipal has been carrying out research since 2014, replacing sustainable stabilizers and reducing synthetic stabilizers. Among the articles already published, 3 publications refer to the study of stabilizers: lignin (CARPENEDO *et al*., 2022) and walnut shell powder (ABATTI *et al*., 2019) (renewable sources), also with reductions in TMQ and 6PPD in formulations for tire retreading products.

According to studies already carried out in the literature, a substitute for 6PPD that presents the same effectiveness has not yet been found. However, the search for new alternatives to keep the properties of elastomeric materials in aged and dynamic conditions for a long period is being evaluated.

4.1 Relevant Factors

According to information by DTSC, 6PPD is toxic towards aquatic organisms at multiple trophic levels. It can impair wildlife survival, as well as being toxic to algae. The chemical compound 6PPD-quinone, a product of the 6PPD reaction, is extremely toxic to coho salmon, including juveniles, and

kills fish within hours of exposure. 6PPD-quinone has been identified as the causal agent of urban runoff mortality syndrome (URMS) observed in the Puget Sound area of Washington State. It kills coho salmon as they migrate upstream, before they are able to spawn. The presence of 6PPD in motor vehicle tires and its release into the aquatic environment has the potential to significantly impact two populations of coho salmon in California: one listed as endangered and the other threatened under the federal Endangered Species Act. The presence of 6PPD-quinone in California runoff and waterways at concentrations above levels that kill at least half of coho salmon in laboratory studies suggests that exposure to 6PPD-quinone may have contributed to the decline of the steelhead population over the past 60-70 years. California's Native American tribes and the state together have invested millions of dollars in an effort to retain and replenish coho populations. The presence of 6PPD-quinone in California's waterways continues to threaten the state's remaining coho salmon populations and may jeopardize the recovery of this species, which faces a number of additional challenges including climate change, habitat destruction and loss, and exposure to other contaminants found in urban runoff. Given the very recent discovery of 6PPD-quinone, little is known about its effects on other aquatic organisms. However, it is potentially toxic to other economically important species that are closely related to coho such as Chinook salmon, steelhead, and the California golden trout. The decline of the coho population has adversely impacted important marine food webs. Coho salmon represent a food source for many marine organisms such as seals and sharks and are a source of ocean-derived nutrients to inland ecosystems. In addition to impacts to aquatic organisms, loss of coho salmon in California has significantly impacted California's Native American tribes. The loss of core traditional food sources for tribal communities can be tied to loss of culture, increased physical and mental health issues, and increased poverty.

4.2 Exposure Paths

4.2.1 Chemical Quantity

Each kg of priority product to be sold in the California market contains approximately 0.5% of 6PPD.

4.2.2 Exposure Factors

Previously, safety data sheets (FDS) were evaluated to verify the properties of the different alternatives proposed in relation to the 6PPD. The information is in the table below:

Properties	6PPD	Lignin	77PD	Irganox 1076
Acute toxicity	Light	No	Harmful	No
Skin corrosion/irritation	Light	No	No	No
Eye injuries	Not available	Light	No	No
Respiratory or skin sensitization	Light	No	Light	No
Mutagenicity	No	No	No	No
Carcinogenicity	No	No	No	No
Reproductive toxicity	No	No	No	No
Single exposure toxicity	No	Light	No	No

Repeated exposure toxicity:	No	No	No	No
Aspiration hazard	No	No	No	No
Environmental toxicity	Very toxic	No	Very toxic	No

4.3 Consideration of Additional Information

Antidegradants to replace, or to reduce 6PPD, must comply with the minimum protection against resistance to ozone, oxygen and temperature currently practiced. Ozone tests must follow the ASTM D 1149 – 2007 standard, comparing standard and test samples under the same conditions: 25 pphm, 24 hours and tensioned, in dynamic testing. Thermo-oxidative aging tests must follow the ASTM D 572 – 04 standard, with forced air circulation and absence of light, for 24, 48 and 72 hours at a temperature of 100°C, comparing standard and test samples under the same conditions, the samples will be tested using test specimens for tear resistance and tension at break. The result must not be lower than the established standard, since it was defined to comply with the validity of the current product, as well as with the technical performance requirements of the product known by users in the market. Internal criteria, which may or may not be shared publicly, use the measurements defined above as well as performance tests that are accepted within the industry. In some cases, performance standards are also legal requirements, as mentioned in item 3.3 for motorcycle tires.

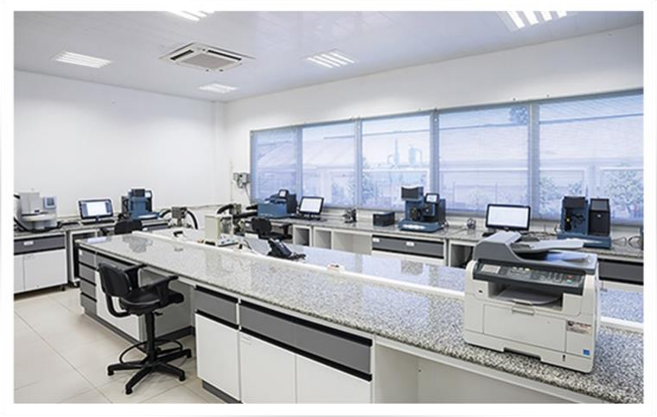
Aging tests to validate or reduce 6PPD in formulations applicable to tire retreading and motorcycle tires, follow the standards below:

- ASTM D 1149, Method A and Method B: Standard Test Method for Rubber Deterioration - Surface Ozone Cracking in a Chamber, USA, 2007.
- ASTM D 572, Method B: Standard Test Method for Rubber - Deterioration by Heat and Oxigen, USA, 2010;
- ASTM G 154: Standard Practice to Operate Fluorescent Light Apparatus for UV Exposure of nonmetallic Materials, USA, 2006.

Part of the tests are carried out at the Vipal company's own Research Center. The Research and Technology Center is located in the city of Nova Prata-RS, Brazil, and aims to evaluate and approve 100% of materials and suppliers. It also evaluates competitors' products and validates new developments and materials from renewable sources.

It is one of the most modern research centers in the world in the tire retreading segment, has 13 laboratories and carries out more than 50 different types of tests, generating more than 28,000 tests annually.

It has 1 researcher with a Post-Doctorate, 2 researchers with a PhD in Engineering and Materials Science, 7 researchers with a Master's degree in Engineering and Materials Science, 2 Chemical Engineers and 5 Chemists, 1 Mechanical Engineer and 2 Production Engineers.



Internal structure of the Vipal Research and Technology Center (CPT) in Nova Prata/RS.

In addition, it has a laboratory called Vipaltec, inside the company, where it carries out tests for certification and research in various segments, including new and retreaded tires. It is accredited by the Inmetro General Accreditation Coordination (CGCRE) and serves tire companies in Brazil and abroad.

Vipal invests in research and academic publications, and already has 17 articles published in renowned journals with high academic impact.

Among these articles we have 3 publications that refer to the study of protectants from renewable sources, lignin, walnut shell powder and also about reductions in TMQ and 6PPD in formulations for tire retreading products.

Secondary tests: after the priority tests have been approved, secondary tests can be carried out as necessary to prove whether the interaction between the antidegradants and the other components of the compound interfere, for example, with adhesion, wear, displacement of components, in migrations and breaks.

5.0 Scope and Comparison of Alternatives

5.1 Alternatives Considered

Vipal is looking for alternatives to solve the problems presented by the use of 6PPD, a. Alternatives will be evaluated in two stages:

1) First stage:

- Reduce up to 10% of the percentage of use of 6PPD in products. It is worth noting that this stage of work is already underway by the company;

2) Second stage:

- Search for alternative molecular products compatible with the stabilization of 6PPD, which are effective in stabilizing the first and second stages of degradation, and which help maintain the stability of breaking sulfur bonds due to aging and maintain stability in materials that undergo action dynamics.
- Alternatives to be evaluated with replacement potential:
  - N,N'-Bis(1,4-dimethylpentyl)-p-phenylenediamine (77PD);
  - N-(1,4-dimethylpentyl)-N'-phenylbenzene-1,4-diamine (7PPD);
  - Ethoxyquin (looking for a supplier);
  - Octadecyl-3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate (Irganox 1076) and other molecules to be evaluated from this supplier;
  - Lignin;
  - NBC—Nickel Dibutyldithiocarbamate (looking for a supplier);
  - Dilauryl Thiodipropionate (looking for a supplier);
  - New molecules that are in the development phase by partner suppliers.

5.2 Rationale for Alternatives not Selected

Vipal understands that IPPD and 6DQDI antidegradants can form 6PPD-quinone as they belong to the PPD family. CCPD is highly toxic for the aquatic environment, the environment and humans. Therefore, it was decided not to study them as priority products.

Due to lower toxicity, antidegradants were selected: lignin, from a natural source, which has several studies on elastomers and Dilauryl Thiodipropionate, which does not yet have applied studies with consistent results, but is less toxic for all media.

77PD/7PPD, despite being part of the 6PPD family, presents medium to low bioaccumulation in the aquatic environment, which is why it was decided to test them.

Ethoxyquin and Nickel Dibutyldithiocarbamate are antidegradants with few applied studies, but with average toxicity when compared to other antidegradants under study. These two protectors will be evaluated.

TMQ is already used in combination with 6PPD. 6PPD is more effective as an antiozonant and TMQ as an antioxidant. Additional tests increasing TMQ and reducing 6PPD were not effective.

5.3 Comparison of Chemical(s) of Concern and Alternative Replacement Chemical(s)

We identify alternative chemicals with potential for use in the manufacture of tire retreading products and motorcycle tires. We do not prioritize potential alternatives or consider technical performance details. We selected alternatives if the source recommended them as having promise as an antidegradant compared to 6PPD, or if they were known for being used as an antidegradant in tires currently or in the past. The GreenScreen® evaluation evaluates 19 danger parameters, not all antidegradants have the information, however Vipal considered products that have less bioaccumulative power in the system to be put into research tests, and in addition to those considered below, other antidegradants may appear for inclusion in these evaluations during the estimated testing period. Below are the 19 parameters considered for inclusion or exclusion of antidegradants:

Group I Human

- Carcinogenicity
- Genotoxicity/mutagenicity
- Reproductive toxicity
- Developmental toxicity
- Endocrine activity

Group II Human

- Acute toxicity
- Systemic toxicity (single dose)
- Systemic toxicity (repeated dose)
- Neurotoxicity (single dose)

• Neurotoxicity (repeated dose)

• Skin sensitization

• Respiratory sensitization

• Skin irritation

• Eye irritation

Ecotoxicity

• Acute aquatic toxicity

• Chronic aquatic toxicity

Destination

• Persistence

• Bioaccumulation

Physical

• Reactivity

• Flammability

The following data is used to assign scores included in the full GreenScreen® report:

• Very low (vL).

• Low (L).

• Moderate (M).

• High (H).

• Very high (vH).

• Data gap (DG), when there is not enough data to assign a score.

Below is information on the antidegradants to be tested, as well as comparative data in relation to 6PPD. Some antidegradants are not listed here, as we are seeking information from suppliers.

Lignin (CAS 8068-05-1)

C = Carcinogenicity	SnR = Respiratory sensitization	SnS = Skin sensitization
M = Mutagenicity	IrS = Skin irritation	CA = Chronic aquatic toxicity
R = Reproductive Toxicity	IrE = Eye irritation	P = Persistence
D = Developmental Toxicity	AA = Acute aquatic toxicity	B = Bioaccumulation
E = Endocrine activity	ST = Systemic toxicity	Rx = Reactivity
AT = Acute mammalian toxicity	N= Neurotoxicity	F= Flammability
DG = Data Gap	L = Low	M = Moderate
H = High	vH = Very High	

Note: Hazard levels L, M, H, vH in *italics* reflect lower confidence values. Hazard levels in **BOLD** font reflect higher confidence values.

Lignin, being from a natural source, is not a PPD-type molecule, therefore it should not be capable of forming a quinone similar to 6PPD-quinone in the aquatic environment. There is no data available on toxicity to Coho salmon, or toxicity to other members of the genus Oncorhynchus. Therefore, the company Vipal must carry out more in-depth research, in addition to existing research published by Carpenedo *et al* (2022) to understand the potential effect of replacing the 6PPD.

7PPD (CAS #3081-01-4)

Group I Human						Group II* and Human								Ecotox		Fate		Physical	
C	M	R	D	E	AT	Systemic toxicity single	Systemic Toxicity repeat*	neurotoxicity single	Neurotoxicity repeat*	SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
L	L	H	M	M	L	L	M	L	DG	H	M	L	M	VH	VH	H	L	L	L

According to studies carried out by ToxServices, 7PPD resulted in BM-1 due to its high reproductive toxicity. Studies on oral exposure in rats identified total loss of litters, longer gestation period and difficult birth, leading to euthanasia in treated women.

The contractor scores 7PPD as high for skin sensitization and persistence. ToxServices identified 7PPD as very high for acute and chronic aquatic toxicity, as it had lethal effect.

It is currently unknown whether 7PPD forms a quinone in the aquatic environment with similar acute toxicity to 6PPD-quinone. A 96-hour LC_{50} is listed on GreenScreen® at 0.4 mg/L for rainbow trout, another member of the Oncorhynchus genus. No data is available for Coho salmon

toxicity. Vipal chose to test and evaluate its performance due to the low bioaccumulation in the system.

77PD (CAS #3081-14-9)

Group I Human						Group II* and Human								Ecotox		Fate		Physical	
C	M	R	D	E	AT	Systemic toxicity single	Systemic Toxicity repeat*	neurotoxicity single	Neurotoxicity repeat*	SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
L	L	L	M	M	L	L	M	L	DG	H	M	L	M	VH	VH	H	M	L	L

C = Carcinogenicity
M = Mutagenicity
R = Reproductive Toxicity
D = Developmental Toxicity
E = Endocrine activity
AT = Acute mammalian toxicity
DG = Data Gap
H = High

SnR = Respiratory sensitization
IrS = Skin irritation
IrE = Eye irritation
AA = Acute aquatic toxicity
ST = Systemic toxicity
N= Neurotoxicity
L = Low
vH = Very High

SnS = Skin sensitization
CA = Chronic aquatic toxicity
P = Persistence
B = Bioaccumulation
Rx = Reactivity
F= Flammability
M = Moderate

Note: Hazard levels L, M, H, vH in *italics* reflect lower confidence values. Hazard levels in **BOLD** font reflect higher confidence values.

According to studies carried out by ToxServices, 77PD was obtained as BM-1 due to its high reproductive toxicity. Studies on oral exposure in rats identified total loss of litters, longer gestation period and difficult birth, leading to euthanasia in treated women. The contractor scores 77PD as high for skin sensitization and persistence.

ToxServices scored 77PD as very high for acute and chronic aquatic toxicity due to the lethal effect on fish with$_{CL50}$ values as low as 0.3 mg/L.

It is currently unknown whether 77PD forms a quinone in the aquatic environment with similar acute toxicity to 6PPD-quinone. A 96-hour LC_{50} is listed on GreenScreen® at 0.4 mg/L for trout and another member of the genus Oncorhynchus. There is no available toxicity data for Coho salmon, however, as it is a similar molecule to 6PPD, it is possible to find Coho salmon quinone and Vipal chose to test the product, as it still presents medium bioaccumulation for the system and low reproduction toxicity.

Group I Human	Group II* and Human	Ecotox	Fate	Physical

C	M	R	D	E	AT	Systemic toxicity single	Systemic Toxicity repeat*	neurotoxicity single	Neurotoxicity repeat*	SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
L	L	L	L	DG	L	L	L	L	DG	L	L	L	L	L	L	L	VL	L	L

Dilauryl Thiodipropionate (CAS #123-28-4)

C = Carcinogenicity	SnR = Respiratory sensitization	SnS = Skin sensitization
M = Mutagenicity	IrS = Skin irritation	CA = Chronic aquatic toxicity
R = Reproductive Toxicity	IrE = Eye irritation	P = Persistence
D = Developmental Toxicity	AA = Acute aquatic toxicity	B = Bioaccumulation
E = Endocrine activity	ST = Systemic toxicity	Rx = Reactivity
AT = Acute mammalian toxicity	N= Neurotoxicity	F= Flammability
DG = Data Gap	L = Low	M = Moderate
H = High	vH = Very High	

Note: Hazard levels L, M, H, vH in *italics* reflect lower confidence values. Hazard levels in **BOLD** font reflect higher confidence values.

According to studies performed by ToxServices, dilauryl thiodipropionate was classified as BM-3DG due to low or very low scores on all endpoints, but with data gaps on endocrine activity and neurotoxicity (repeated dose). These data gaps prevent the assignment of a BM-4 score, resulting in the BM-3DG classification. To achieve a BM-4 score, data on all endpoints is required. The hazard assessment classified dilauryl thiodipropionate as low risk for acute and chronic aquatic toxicity due to low toxicity at all three trophic levels (fish, invertebrates and algae). Dilauryl thiodipropionate is not a PPD-type molecule, therefore it should not be able to form a quinone similar to 6PPD-quinone in the aquatic environment. There is no data available on toxicity to Coho salmon or on toxicity to other members of the genus Oncorhynchus.

Dilauryl thiodipropionate (DLTDP) acts as an antioxidant for the decomposition of hydroperoxides formed in the second stage of degradation. Therefore, it requires auxiliary protective co-agents, which are primary to be efficient in the degradation and aging process of technical tire products.

P● + XH → PH + X● (1)

POO● + XH → PO-OH + X● (2)

This material presents few studies on the application of tires and their retreading products for an effective antioxidant and antiozonant. Studies need to be carried out.

C	M	R	D	E	AT	Systemic toxicity single	Systemic Toxicity repeat*	neurotoxicity single	Neurotoxicity repeat*	SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
L	L	M	M	M	M	VH	H	DG	DG	L	DG	L	L	H	H	H	VL	L	L

Ethoxyquin (EQ, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline) (CAS #91-53-2)

C = Carcinogenicity	SnR = Respiratory sensitization	SnS = Skin sensitization
M = Mutagenicity	IrS = Skin irritation	CA = Chronic aquatic toxicity
R = Reproductive Toxicity	IrE = Eye irritation	P = Persistence
D = Developmental Toxicity	AA = Acute aquatic toxicity	B = Bioaccumulation
E = Endocrine activity	ST = Systemic toxicity	Rx = Reactivity
AT = Acute mammalian toxicity	N= Neurotoxicity	F= Flammability
DG = Data Gap	L = Low	M = Moderate
H = High	vH = Very High	

Note: Hazard levels L, M, H, vH in *italics* reflect lower confidence values. Hazard levels in **BOLD** font reflect higher confidence values.

According to ToxServices, ethoxyquin was classified as BM-2 due to high persistence, moderate group I toxicity (reproductive, developmental and endocrine activity) and very high systemic toxicity (single dose). Ethoxyquin had effects on litter number, gestation length, and pup body weight in rats, although at higher doses it also caused maternal toxicity. Ethoxyquin has been shown to have some effect on androgenic activity in vitro, although it is unclear whether this leads to any potential health effects. Ethoxyquin was lethal to rats with LD_{50} of 800 mg/kg. Dogs given a single dose of 100 mg/kg or 2 mg/kg/day saw a change in blood chemistry, leading to liver damage. ToxServices identified data gaps on neurotoxicity (single and repeated exposure) as well as respiratory sensitization. Ethoxyquin was classified as high risk for persistence, but this was based on modeled data, so a low confidence score was assigned. Ethoxyquin has not been shown to be as toxic to aquatic organisms as 6PPD, with the most conservative value identified at 2 mg/L in water fleas, although it is still considered a high risk for acute and aquatic toxicity. Ethoxyquin is not a PPD like many of the other compounds evaluated, so it is unlikely to form a transformation product similar to 6PPD-quinone, which is much more toxic to Coho salmon. There is no data on the toxicity of ethoxyquin to Coho salmon, but it has a listed LC_{50} of 18 mg/L for rainbow trout, another member of the Oncorhynchus genus.

Ethoxyquin has few studies in elastomers as an antiozonant and antioxidant. Studies need to be carried out to better understand its performance.

NBC—Nickel Dibutyldithiocarbamate (CAS #13927-77-0).

Group I Human						Group II* and Human								Ecotox		Fate		Physical	
C	M	R	D	E	AT	Systemic toxicity single	Systemic Toxicity repeat*	neurotoxicity single	Neurotoxicity repeat*	SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
H	L	M	L	DG	L	L	H	M	L	L	M	L	H	L	L	VH	L	L	L

C = Carcinogenicity
M = Mutagenicity
R = Reproductive Toxicity
D = Developmental Toxicity
E = Endocrine activity
AT = Acute mammalian toxicity
DG = Data Gap
H = High

SnR = Respiratory sensitization
IrS = Skin irritation
IrE = Eye irritation
AA = Acute aquatic toxicity
ST = Systemic toxicity
N= Neurotoxicity
L = Low
vH = Very High

SnS = Skin sensitization
CA = Chronic aquatic toxicity
P = Persistence
B = Bioaccumulation
Rx = Reactivity
F= Flammability
M = Moderate

Note: Hazard levels L, M, H, vH in *italics* reflect lower confidence values. Hazard levels in **BOLD** font reflect higher confidence values.

According to ToxServices, NBC was classified as BM-1 due to very high persistence, high carcinogenicity and high systemic toxicity (repeated dose). NBC has been classified as high in terms of carcinogenicity due to multiple official listings of nickel compounds as a carcinogenic group. However, due to an 18-month study in rats that showed negative carcinogenicity results, this final score was considered low confidence. ToxServices did not consider the 18-month study sufficient to overturn an official listing, as two-year studies are standard in carcinogenicity investigations. The evaluation classified NBC as high for systemic toxicity (repeated dose), due to the effects on the heart and skeletal muscle that occur at 2 mg/kg/day. Due to the presence of an inorganic metal, NBC is expected to be recalcitrant in the environment. A test on activated sludge confirms this, but the very high persistence score has received low confidence due to a lack of experimental data. ToxServices identified a data gap in endocrine activity. Acute and chronic aquatic toxicity was low in the identified data and NBC received a low risk score for these parameters. NBC is not capable of forming a quinone in the aquatic environment as it is not a PPD, but specific toxicity to Coho salmon is unknown. Toxicity to rainbow trout, another member of the Oncorhynchus genus, was greater than 100 mg/L in the ECOTOX database.

Nickel Dibutyldithiocarbamate has few studies in elastomers as an antiozonant and antioxidant. Studies need to be carried out to better understand its performance.

It is understood that the antidegradants IPPD and 6DQDI can form a 6PPD-quinone as they belong to the PPD family. CCPD is highly toxic for the aquatic environment, the environment and humans. Therefore, it was decided not to study them as priority products.

Due to lower toxicity, we have selected the antidegradants: lignin, from a natural source, which has several studies on elastomers and Dilauryl Thiodipropionate, which does not have applied studies with consistent results yet, but is less toxic for all media.

77PD/7PPD, despite being part of the 6PPD family, has medium to low bioaccumulation in the aquatic environment, which is why Vipal decided to test them.

Ethoxyquin and Nickel Dibutyldithiocarbamate are antidegradants with few applied studies, but with average toxicity when compared to other antidegradants under study.

TMQ is already used in combination with 6PPD. 6PPD is more effective as an antiozonant and TMQ as an antioxidant. Additional tests increasing TMQ and reducing 6PPD were not effective.

6.0 SELECTED ALTERNATIVE(S)

As described in item 5.0.

7.0 WORK PLAN

7.1 Discussion of Proposed Tasks to Generate the Final AA Report

In accordance with the new regulations informed by the DTSC, the company Vipal, one of the largest manufacturers of rubber products worldwide and motorcycle tires, has always sought to offer its customers the most advanced technologies, always improving its products. All necessary actions foreseen in the agenda of the new regulation are already being handled and prepared internally, so that the transit and commercialization of our products in that state are not affected. Considering that the path to innovation is constantly evolving, the team of experts has been conducting research focused on the scope of this regulation for some years. Confident that our products will meet the required regulatory requirements, delivering total security and reliability to our customers, we reaffirm our commitment to quality and below we highlight the proposed work plan to comply with the regulations in question. The initial proposal is to divide the study into two stages:

1) First stage:

- Reduce up to 10% of the percentage of use of 6PPD in products. It is worth noting that this stage of work is already underway by the company;

2) Second stage:

- Search for alternative molecular products compatible with the stabilization of 6PPD, which are effective in stabilizing the first and second stages of degradation, and which help maintain the stability of breaking sulfur bonds due to aging and maintain stability in materials that undergo action dynamics.
- Alternatives to be evaluated with replacement potential:
  - N,N’-Bis(1,4-dimethylpentyl)-p-phenylenediamine (77PD);
  - N-(1,4-dimethylpentyl)-N'-phenylbenzene-1,4-diamine (7PPD);
  - Ethoxyquin;
  - octadecyl-3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate (Irganox 1076);

- Lignin;
- NBC—Nickel Dibutyldithiocarbamate;
- Dilauryl Thiodipropionate;
- New molecules that are in the development phase by partner suppliers.

Item 7.2 lists the schedule of proposed activities.

7.2 Proposed Implementation Schedule

Proposal 1: Reduction in the percentage of 6PPD in the listed products:

Action Item	Description	Scheduled Completion Date
1	Study to reduce the percentage of 6PPD by 10 % in listed products	12 months

Proposal 2: Search for alternative potentials aimed at replacing 6PPD in the listed products:

Action Item	Description	Scheduled Completion Date
1	Purchase alternative materials	3 months
2	Test, on a laboratory scale, including evaluating in an oxidative/ozone chamber and dynamic tests	5 months
3	Validate in the field	2 months
4	Evaluate results obtained	1 month
5	Prepare PAA	1 month

It is Vipal's commitment to promote, together with the supply chain, new and better solutions to protect rubber and cause less environmental impact.

We are monitoring, together with the main global suppliers, any new alternative that fulfills the function of replacing the 6PPD, keeping its same current performance, aiming to guarantee the same current durability. Thus, avoiding an increase in waste generation due to faster aging and disposal of our rubber products.

To support this work, the company invested in its Research and Technology Center (CPT), providing resources and qualified staff to test and technically approve the best alternatives to be used in rubber products.

REFERENCES

ABATTI, L.; VIEIRA, E. R.; DA SILVA CRESPO, J. Thermal evaluation of rubber compounds containing pecan nutshell powder for tire treads. *Journal of Thermal Analysis and Calorimetry*, v. 138, n. 5, p. 3673-3678, 2019.

ASTM D 1149, Method A: Standard Test Method for Rubber Deterioration - Surface Ozone Cracking in a Chamber, EUA, 2007.

ASTM D 572, method B: Standard Test Method for Rubber - Deterioration by Heat and Oxigen, USA, 2010.

ASTM G 154: Standard Practice to Operate Fluorescent Light Apparatus for UV Exposure of nonmetallic Materials, USA, 2006.

CARPENEDO, G.A. *et al*. Evaluation of Stabilizing Additives Content in the Mechanical Properties of Elastomeric Compositions Subject to Environmental and Accelerated Aging. *Materials Research*. 23 (5). 2020. https://doi.org/10.1590/1980-5373-MR-2020-0139.

CARPENEDO, G. A. *et al*. Evaluation of lignin as stabilizer in vulcanized natural rubber formulations. *Polímeros: Ciência e Tecnologia,* 32(3), 2022. https://doi.org/10.1590/0104-1428.

Dweik, H.S.; G. Scott, Rubber Chem. Technol., 57, (1984), 735.

GUGUMUS, F. Oxidation inhibition in organic materials, CRC Press ed., v.1, 1990.

MAUSS, C. J. *e al*. Antioxidant effect of lignin in elastomeric compounds for tire tread. Master's Thesis in Mining, Metallurgical and Materials Engineering. Porto Alegre, 2020.

RAPTA P. *et al*. A variety of oxidation products of antioxidants based on N,N0-substituted p-phenylenediamines, *Polymer Degradation and Stability*, v.94, p.1457-1466, 2009.