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Exploration of Green Alternatives to 6PPD (P-Phenylenediamine) Used as Antiozonant and Antioxidant in the Rubber Industry

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Abstract

Antiozonants and antioxidants are additives commonly used in the rubber industry to enhance the durability and performance of rubber products. Ozone, present in the atmosphere, can cause rubber to degrade over time through a process known as ozone cracking. These rubber additives are added to rubber compounds to protect against this degradation. They work by reacting with ozone, preventing it from attacking and breaking the molecular chains in the rubber, helping to maintain the structural integrity of the rubber product. It is now well known that 6PPD contributes to the extension of the service life of rubber products. However, recent studies have shown that 6PPD can be harmful to the environment, especially when end-of-life tyres (ELTs) are contaminated with the water. With the effect of ozone, 6PPD is converted to 6PPD quinone, which is toxic enough to kill some sensitive fish species such as Coho Salmon (*Oncorhynchus kisutch*). This study drew attention to new chemical compounds and natural products that can be used as antiozonants and antioxidants in the rubber industry instead of 6PPD. Although the scientific studies are promising, the fact that 6PPD is still used in production shows that more scientific studies and social awareness need to be developed in this area.

Keywords

6PPD, Coho Salmon, Antiozonant, Antioxidant

1. Introduction

Hevea brasiliensis is the primary source of natural rubber (NR). These trees are grown in regions with tropical climates such as South East Asia, Africa and South America (**Figure 1**) [1]. Total rubber consumption increased by 61.2% from 2000 to 2014, and demand continues to grow. In 2014, global NR consumption reached 12,159 megatonnes, an increase of nearly 6.8% over the previous year, and consumption is expected to continue growing due to increasing demand from emerging economies such as China, India and Brazil. Global NR consumption is expected to reach 16.5 mt/y by 2023 and continue to grow thereafter [2].

The compounded rubber is then processed into various end products using methods such as extrusion, calendering, and moulding (**Figure 2**) [3].

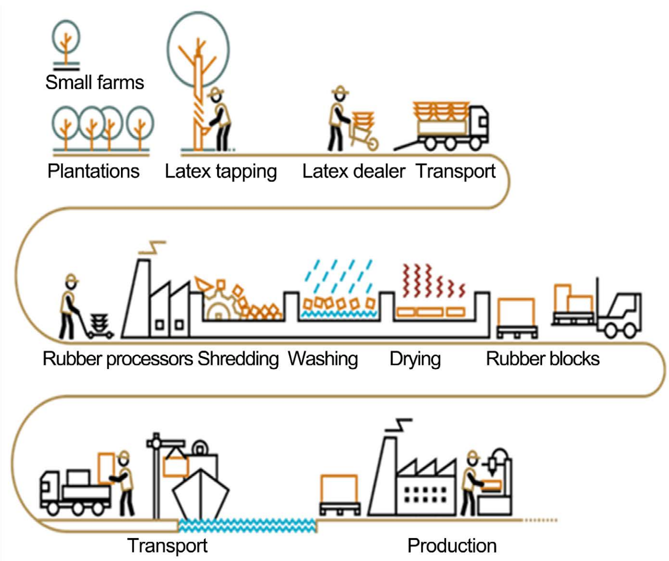

Figure 1. Natural rubber supply process.

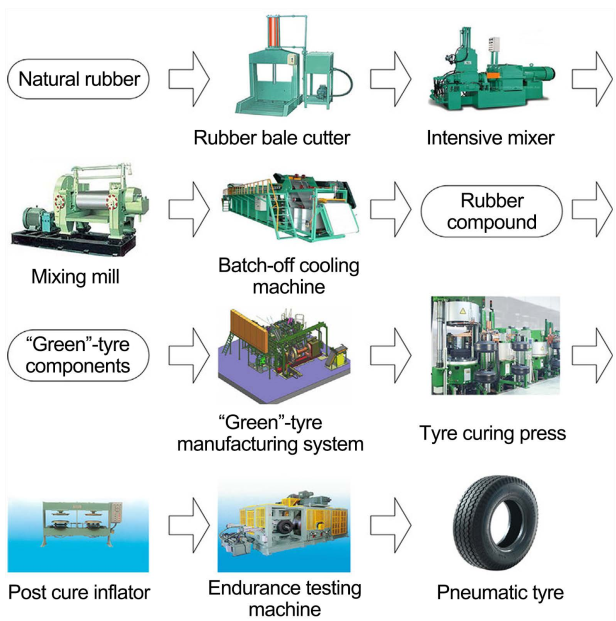

Figure 2. The flow of operations in the entire tyre-manufacturing system.

In the manufacturing process, rubber compounds are produced by mixing natural rubber with various additives. These additives include fillers, accelerators, antiozonants, antioxidants, activators, stabilisers, pigments and sometimes synthetic rubber [4]. These chemical additives play a critical role in improving the performance, durability and processing characteristics of rubber [5].

The rubber additives market size was valued at $5879 million in 2022 and is expected to reach $9136 million by 2030 (**Figure 3**) [6]. It is quite remarkable that this market will have a growth rate of over 55% in 8 years.

Important chemical additives used in the rubber industry are briefly mentioned below;

1.1. Fillers

Carbon black and silica are both commonly used as fillers in rubber compounds. While carbon black improves strength, abrasion resistance and UV resistance, silica serves as an alternative with benefits such as improved fuel efficiency and wet traction in tyres.

1.2. Vulcanizing Agents

The most commonly used vulcanising agent (**Figure 4**) in rubber compounding is sulphur. When combined with accelerators, sulphur forms cross-links between polymer chains, resulting in improved strength, elasticity and durability [7].

Figure 3. Standard additives used in the rubber industry.

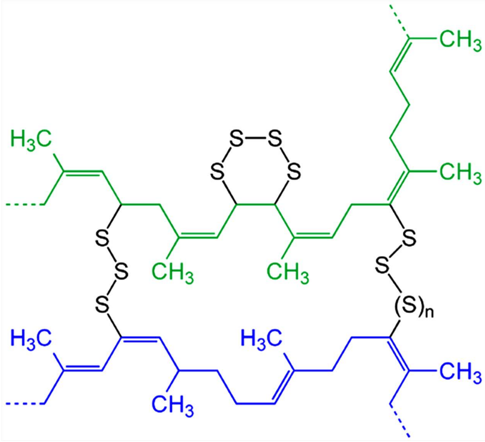

Figure 4. Chemical reaction of the vulcanization process.

1.3. Accelerators

Substances such as accelerators (e.g., thiurams, thiazoles) are added to speed up the vulcanization process.

1.4. Plasticizers

Plasticizers (e.g., oils, resins) are used to improve the flexibility and workability of rubber compounds. They are particularly important in applications where flexibility is critical, such as in the production of rubber hoses and belts.

1.5. Softeners

Softeners are substances that increase the flexibility and softness of rubber. They are often used in applications where a softer rubber is desired, such as in the production of seals and gaskets.

1.6. Stabilizers

Stabilisers are added to rubber compounds to prevent degradation during processing and exposure to heat and UV light. Zinc oxide (ZnO) is a compound widely used as a stabiliser in the rubber industry. Zinc oxide adds strength to rubber compounds, improves their resistance to heat/abrasion and helps protect against ultraviolet degradation (**Figure 5**) [8].

1.7. Colorants

Pigments and dyes are used as colorants to give rubber products the desired colour. This is particularly important in applications where aesthetics is important, such as consumer goods.

1.8. Antioxidants

Antioxidants (e.g. phenols, amines) are added to protect rubber from oxidising agents (such as oxygen) heavy metals, UV rays, ozone, mechanical stress, heat and aggressive chemicals, etc. can accelerate rubber ageing [9] [10].

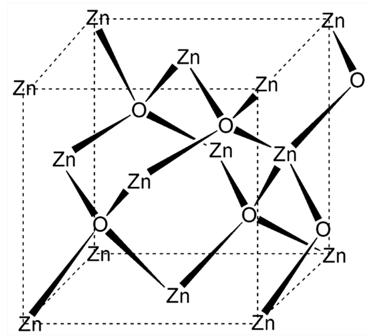

Figure 5. Molecule structure of ZnO.

The commonly used rubber antioxidant can be divided into primary antioxidant and secondary antioxidant according to the anti-aging mechanism. The primary antioxidants, such as aryl amines and phenolic antioxidants, could inhibit the propagation reaction by providing the reactive hydrogen atom to the free radicals. The primary antioxidants are generally thermostable and are incorporated into the rubber matrix during the mixing stage. In contrast, secondary antioxidants, including phosphites, thiols and organic sulfides, can reduce hydroperoxide radicals to the corresponding alcohols. The secondary antioxidants are not thermostable and are generally used to stabilise rubber systems during the solution phase of manufacture. In general, the primary antioxidants and secondary antioxidants can be used together to protect the rubber as they could have a synergistic antioxidant effect, *i.e.* the primary antioxidant could be used as a chain-breaking donor type to trap the free radical during the oxidation ageing period and the secondary antioxidant could react with the hydroperoxide by-product, and their combination has been regarded as one of the most effective and popular antioxidant combinations in the rubber industry [11].

1.9. Antiozonants

These additives protect rubber from ozone degradation, which can cause surface cracking. Antiozonants react with ozone, preventing it from attacking and breaking down the polymer chains in rubber.

Under deformation, vulcanisates susceptible to ozone attack have a critical elongation below which cracks will not form. However, the incorporation of antiozonants into the compound provides a significant improvement in resistance to ozone attack. They work by migrating from the bulk of the vulcanisate to the surface where they react preferentially with the ozone, thereby protecting the integrity of the component. The most commonly used antiozonants are the substituted para-phenylenediamines. As well as providing protection against ozone, they also act as antioxidants and are excellent anti-fatigue agents [12] [13].

2. The Usage of 6PPD (P-Phenylenediamine) in the Rubber Industry

6PPD is widely produced and used in many commercial rubber products; including car tyres, rubber hoses and belts. These chemicals offer exceptional protective capabilities for safeguarding rubber products from heat deterioration, degradation, and ozone-induced cracking, working as antioxidants [14].

When 6PPD is exposed to air, it reacts with ozone to form 6PPD-quinone, pronounced "qui-KNOWN" and also known as 6PPDQ (**Figure 6**). 6PPDQ is a toxicant that has been found in roadway runoff and receiving water systems.

The estimated tyre production in 2019 was about 16.86 million tons and is expected to grow 5% - 7% each year [15]. Tyre wear particles, which are generated by friction between vehicles and the road surface, have recently attracted attention for their impact on the environment.

Tyre wear particles are rubber-based product similar to micro plastics that can be transported and dispersed into the environment, including air, water and soil, by various mechanisms such as saltation, abrasion of larger particles, the sheer force of moving air and water (**Figure 7**) [16] [17].

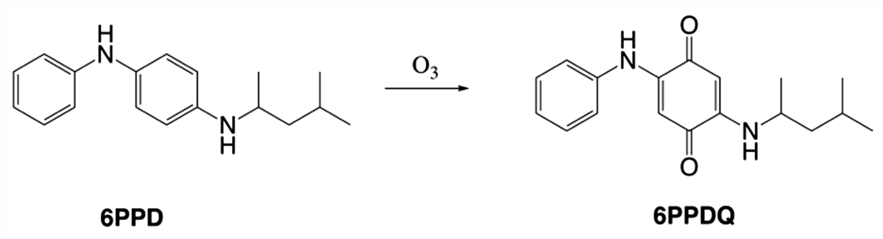

Figure 6. Converting reaction of 6PPD to 6PPDQ.

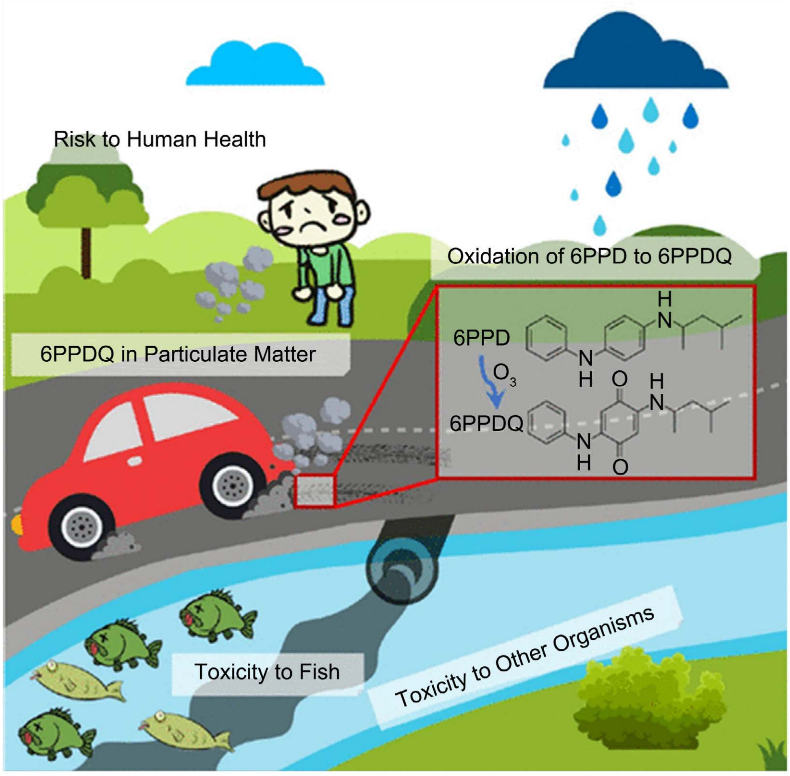

Figure 7. Impact of tyre wear particles on nature.

Scientific studies show that 6PPDQ is lethal to coho salmon and other sensitive special fish species. Coho Salmon is the most popular of the wild salmon among smokers in Europe. Its medium size and the appealing color of its meat also make it very popular with restaurateurs (**Figure 8**) [18]. Several distinct wild populations of Coho, steelhead and Chinook salmon are currently protected under the U.S. Endangered Species Act (ESA) in California and the Pacific Northwest. Conservation of these protected species is generally managed at the population level, which requires consideration of cumulative losses across all life stages due to exposure to toxic urban runoff [19].

With increasing urbanization, rainfall previously absorbed into the soils of forests and grasslands falls instead on pavement and other hardened surfaces. This creates storm water runoff that carries toxic metals, oil, and many other contaminants into salmon bearing habitats. These include freshwater streams where Coho Salmon spawn in gravel beds.

Coho salmon embryos develop inside a thick eggshell (chorion) for weeks to months before hatching out as alevins and finally emerge from the gravel as fry. Untreated urban runoff is highly toxic to older Coho salmon (freshwater resident juveniles and adult spawners) [20].

The extensive use of 6PPD particularly in tyres significantly results in its frequent detection in various environmental matrices, including municipal wastewater treatment plants, urban runoff, and air particles with concentrations of 11.2 - 14.3 μg/L, 0.21 - 2.71 μg/L, 1.02 - 9340 pg/m^3. In parallel, 6PPD has been proved to be toxic to aquatic organisms such as the China-specific *Gobiocypris rarus* and zebrafish larvae, with median 96 h median lethal concentrations of 162 μg/L and 443 μg/L, respectively [21].

The cause of mortality of coho salmon by assuming the transformation of 6PPD in the environment by ozonation to become 6PPDQ, where the quinone form was found to be highly toxic at a lethal dose of 0.8 - 0.16 μg/l. The precursor compound 6PPD is mainly comes from tyre wear particles, which is used as an antioxidant and antiozonant to protect tyres and extend their life [22].

3. Findings and Discussion

Unfortunately, 6PPD has been used extensively in the rubber industry despite the damage it causes to the environment and living things. Therefore, it is very important to develop methods to reduce the environmental hazards of tyre antioxidants. Alternative chemicals that can replace this product are proposed below.

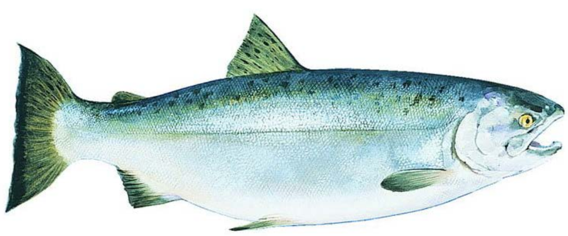

Figure 8. Coho Salmon (*Oncorhynchus kisutch*).

3.1. The Use of Modified 6PPD

Yu Wang *et al*. reported that certain concentrations of tyre antioxidants such as 6PPD can cause acute toxicity in aquatic salmonids. Density functional theory (DFT) was used to analyse the design of environmentally friendly derivatives of 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ). The authors determined the most ecological and effective TMQ structure by designing 70 different molecules. This study can also be carried out for 6PPD [23].

3.2. The Use of N, N'-Diphenyl-P-Phenylenediamine (DPPD) Instead of 6PPD

DPPD is used as a polymerization inhibitor and antioxidant (Figure 9). The antioxidative activity of DPPD is implemented by the donation of a hydrogen to a radical derivative and breaking the autocatalytic cycle. DPPD is widely used in rubber, oils, and feed stuffs, especially for tyres in the rubber industry due to its color and stability [24].

DPPD has a higher melting point than 6PPD, which is used in the rubber industry for the same properties. DPPD melts at 140˚C, while 6PPD melts at 46˚C. This difference provides a significant advantage in the heat transfer of the additive material, which makes up 14% of the passenger car tyre by mass (Figure 10), to the environment. There are also studies showing that DPPD is less toxic.

DPPD molecule reacts with ozone and turns into DPPD-quinone molecule over time (Figure 11). While the lipid solubility (LogKow) of this molecule is 3.46, the LogKow of the 6PPD-quinone molecule is 3.98. In other words, 6PPD-quinone is more soluble in oil. The 6PPD-quinone molecule, which is more soluble in the oils used in the production process, is released into enviroment.

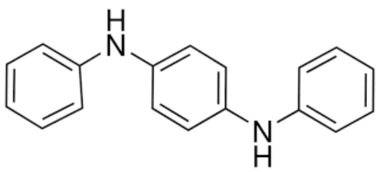

Figure 9. Structure of DPPD.

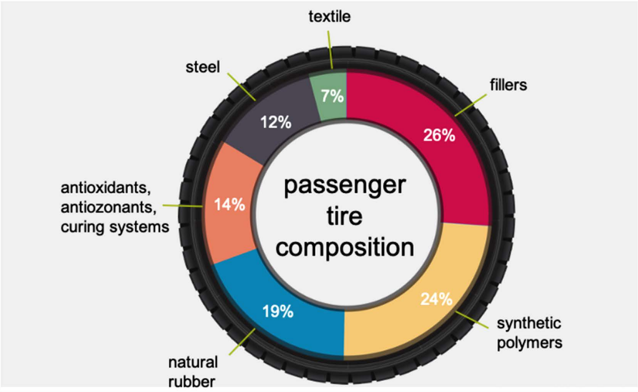

Figure 10. Chemical composition of passenger tyre [25].

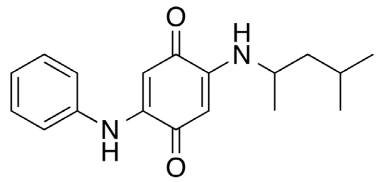

Figure 11. Structure of 6PPD-quinone.

3.3. The Use of Food Preservative-Gallates Instead of 6PPD

Food preservatives such as gallates (**Figure 12**) (including propyl gallate, octyl gallate and dodecyl gallate) are commonly used to prevent spoilage and extend the shelf life of food. They are antioxidants that inhibit the oxidation of fats and oils, helping to maintain the quality and freshness of foods [26] [27].

Gallates are selected for their ability to prevent lipid oxidation and extend the shelf life of foods, while 6PPD is used to protect rubber products from oxidative degradation.

6PPD has a half-wave redox potential of −0.12 V against the same quasi-reference electrode, indicating that it is a stronger reducing agent than the range of gallates tested. Nevertheless, the gallate compounds tested have a redox potential below that of singlet oxygen (0.8 V), suggesting that the gallates tested could adequately quench reactive oxygen species that could lead to tyre degradation [28].

In terms of antiozonant activity, a scientific study of biological systems suggests that propyl gallate may protect against damage caused by its reaction with ozone [29]. This study shows that propyl gallate can protect against ozone damage. A thorough study of this compound in a rubber matrix will be necessary to understand the full potential of its antioxidant and anti-ozonant properties and how these compare with 6PPD. In order for the gallate compound to perform its antidegradant functions, it must diffuse to the rubber surface where it can react with oxidants. If an antidegradant compound diffuses too slowly, it may not adequately protect the tyre surface from oxidation and ozone. If it diffuses too quickly, the antidegradant may be depleted too quickly, shortening the life of the tyre [30].

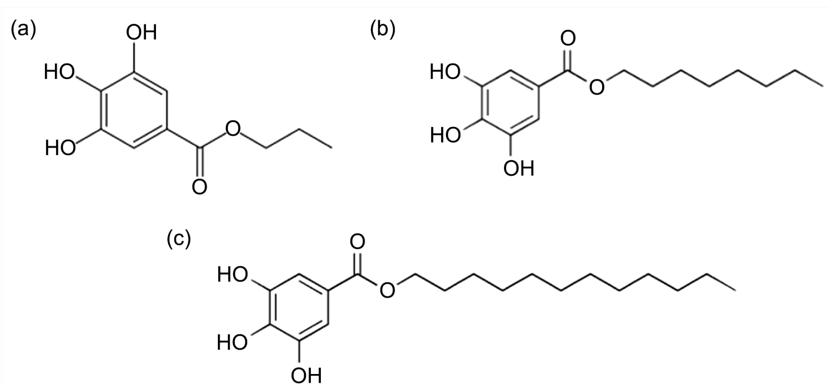

Figure 12. (a) propyl gallate, (b) octyl gallate, (c) dodecyl gallate.

The fact that there are very limited studies on the use of gallates as antiozonants in the rubber industry causes us to obtain indirect information about these compounds. The LogKow values of propyl gallate are 2.3, octyl gallate 3.5 and dodecyl gallate 4.5, respectively [31] [32]. In this case, propyl gallate can be recommended to be used instead of 6PPD. However, more research should be done in this area.

3.4. The Use of Lignin Instead of 6PPD

Lignin is one of the most abundant components in the biosphere. It is a natural polymeric antioxidant with phenolic functionality. Commercial lignin is mainly extracted in large quantities as a by-product of pulp production during delignification [33].

Lignin is a three-dimensional amorphous natural polymer consisting of phenylpropane units with carbonyl, hydroxyl and methoxyl substituents. Lignins are found in plants and act as stabilisers against mechanical, biochemical and environmental stresses [34].

The specific properties and characteristics of lignin can be highlighted as being widely available, naturally non-hazardous and biodegradable, thus environmentally friendly and non-toxic, unlike the organic antioxidants used in current industries [35].

Lignin has the property of being used as an antioxidant and filler for rubber and can be used as a potential source in biodiesel production [36].

Nowadays, the incorporation of lignin into various polymeric materials has received more attention due to some of its properties such as cross-linked structure with tetrafunctional branching points, strong intramolecular interactions, processability, stabilising effect, reinforcing effect and biodegradability (**Figure 13**) [37] [38]. It has many properties such as good mechanical, physico-chemical, biodegradability, antioxidant properties and excellent thermal stability [39].

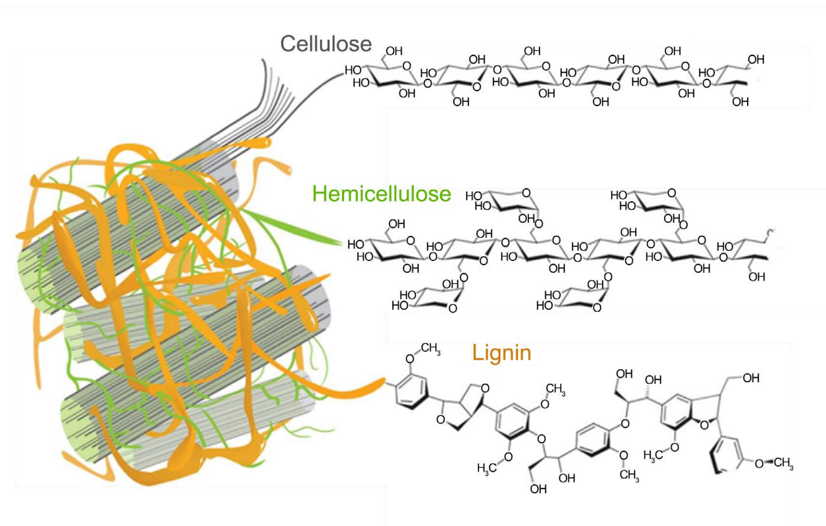

Figure 13. Chemical structure of Cellulose, Hemicellulose and Lignin.

Carpenedo *et al*. investigated the use of lignin as a stabiliser in a blend containing natural rubber. 6PPD showed significantly greater resistance to oxidative degradation than other materials such as TMQ [40].

Gregorova *et al*. investigated lignin with respect to thermo-oxidative ageing in blends containing carbon black and natural rubber. The mechanical properties and cross-link density of lignin stabilised vulcanisates were tested before and after thermo-oxidative ageing at 80˚C for 24, 72, 168, 240 and 408 hours. The results showed a stabilising effect compared to synthetic antioxidants [41].

4. Conclusions

6PPD has been used for many years as an antiozonant and antioxidant in the rubber-processing industry. Unfortunately, recent studies show that it has been found to be toxic to coho salmon and other aquatic organisms. When tyres break down on the road, 6PPD leaches into nearby waterways. This poses a threat to aquatic life.

The number of chemical compounds in a car tyre is approximately 20 - 30. This number can be changed due to the specific formulation used by the tyre manufacturer. The complex formation process has been determined as a result of serious R&D studies. The impact of a small change in the formula on the tyre to be produced is made according to the results obtained after the research and the prototyping. Even if laboratory studies give positive results, the feedback from real-life conditions can sometimes be very different from laboratory data. That's why manufacturers don't want to change the formula they use.

This study has drawn attention to products that have the potential to be used as alternatives to 6PPD in the rubber industry. However, not enough scientific studies have been found proving that these products can be used in the formulations of currently used tyres.

It is not yet fully known at what dose 6PPD is harmful to other living organisms other than coho salmon and even to humans. It seems that these investigations will take a long time. The scientist therefore has a great responsibility.

In order to increase the number of scientific studies in this field, legislators should allocate large economic resources and encourage scientific studies. Updated regulations limiting the use of chemicals such as 6PPD should be published by a certain date. Processes, procedures and technologies need to be regularly reviewed and updated to minimise the use of hazardous chemicals and improve overall safety and sustainability.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Dialogue with Natural Rubber Suppliers Continues. https://www.trelleborg.com/en/sustainability/sustainability-news/dialogue-with-natural-rubber-suppliers-continues

[2] Cornish, K. (2017) Alternative Natural Rubber Crops: Why Should We Care? *Technology & Innovation*, **18**, 244-255. https://doi.org/10.21300/18.4.2017.245

[3] Jovanović, M., Zupan, S., Starbek, M. and Prebil, I. (2014) Virtual Approach to Holonic Control of the Tyre-Manufacturing System. *Journal of Manufacturing Systems*, **33**, 116-128. https://doi.org/10.1016/j.jmsy.2013.07.005

[4] Altundal, G., Gerengi, H., Çetin, E., Kapcak, U. and Kaymaz, K. (2020) Performans Bisiklet Lastiği Sırt Karışımının Geliştirilmesi Ve Özelliklerinin İncelenmesi. *Düzce Üniversitesi Bilim ve Teknoloji Dergisi*, **8**, 1661-1675. https://doi.org/10.29130/dubited.698101

[5] Demir, E., Altundal, G., Gerengi, H. and Yüksel, C. (2023) Investigation of the Potential of Using Liquid Rubbers in Rubber Industry. *Journal of Materials Science and Chemical Engineering*, **11**, 21-30. https://doi.org/10.4236/msce.2023.119002

[6] Market Reports Insights. https://www.marketreportsinsights.com/sample/173358

[7] Sulfur Vulcanization. https://en.wikipedia.org/wiki/sulfur_vulcanization

[8] Zinc Oxide. https://www.acs.org/molecule-of-the-week/archive/z/zinc-oxide.html

[9] Kane, A., Diakhaté, P.A., Ndao, S., Dieng, M., Cisse, M. and Diop, A. (2024) Identification of Antioxidant Additives in Food Products Sold in Dakar Markets. *Open Journal of Applied Sciences*, **14**, 51-62. https://doi.org/10.4236/ojapps.2024.141004

[10] De Oliveira, C.T. and Tavares, M.I.B. (2022) Antioxidant and Cytotoxic Activities of Clove Oil Nanoparticles and Evaluation of Its Size and Retention Efficiency. *Materials Sciences and Applications*, **13**, 39-53. https://doi.org/10.4236/msa.2022.131003

[11] Zhao, W., He, J., Yu, P., Jiang, X. and Zhang, L. (2023) Recent Progress in the Rubber Antioxidants: A Review. *Polymer Degradation and Stability*, **207**, Article ID: 110223. https://doi.org/10.1016/j.polymdegradstab.2022.110223

[12] Huntink, N.M., Datta, R.N., Talma, A. and Noordermeer, J.W. (2006) Ozonolysis of Model Olefins—Efficiency of Antiozonants. *Journal of Applied Polymer Science*, **100**, 853-866. https://doi.org/10.1002/app.22861

[13] Datta, R.N. and Ingham, F.A.A. (2001) Rubber Additives—Compounding Ingredients. In: White, J.R. and De, S.K., Eds., *Rubber Technologist's Handbook*, Rapra Technology Ltd., Shawbury, 167-208.

[14] Liu, R. and Mabury, S.A. (2020) Synthetic Phenolic Antioxidants: A Review of Environmental Occurrence, Fate, Human Exposure, and Toxicity. *Environmental Science & Technology*, **54**, 11706-11719. https://doi.org/10.1021/acs.est.0c05077

[15] Bijina, V., Jandas, P.J., Joseph, S., Gopu, J., Abhitha, K. and John, H. (2023) Recent Trends in Industrial and Academic Developments of Green Tyre Technology. *Polymer Bulletin*, **80**, 8215-8244. https://doi.org/10.1007/s00289-022-04445-2

[16] Zoroufchi Benis, K., Behnami, A., Minaei, S., Brinkmann, M., McPhedran, K.N. and Soltan, J. (2023) Environmental Occurrence and Toxicity of 6PPD Quinone, an

Emerging Tire Rubber-Derived Chemical: A Review. *Environmental Science & Technology Letters*, **10**, 815-823. https://doi.org/10.1021/acs.estlett.3c00521

[17] Bohara, K., Timilsina, A., Adhikari, K., Kafle, A., Basyal, S., Joshi, P. and Yadav, A.K. (2023) A Mini Review on 6PPD Quinone: A New Threat to Aquaculture and Fisheries. *Environmental Pollution*, **340**, Article ID: 122828. https://doi.org/10.1016/j.envpol.2023.122828

[18] Coho Salmon (*Oncorhynchus kisutch*). https://alaskaseafood.site/alaska-products/wild-salmon/coho-salmon/

[19] McIntyre, J.K., Spromberg, J., Cameron, J., Incardona, J.P., Davis, J.W. and Scholz, N.L. (2023) Bioretention Filtration Prevents Acute Mortality and Reduces Chronic Toxicity for Early Life Stage Coho Salmon (*Oncorhynchus kisutch*) Episodically Exposed to Urban Stormwater Runoff. *Science of the Total Environment*, **902**, Article ID: 165759. https://doi.org/10.1016/j.scitotenv.2023.165759

[20] Du, B., Lofton, J.M., Peter, K.T., Gipe, A.D., James, C.A., McIntyre, J.K. and Kolodziej, E.P. (2017) Development of Suspect and Non-Target Screening Methods for Detection of Organic Contaminants in Highway Runoff and Fish Tissue with High-Resolution Time-of-Flight Mass Spectrometry. *Environmental Science: Processes & Impacts*, **19**, 1185-1196. https://doi.org/10.1039/C7EM00243B

[21] Li, C., Zhang, Y., Yin, S., Wang, Q., Li, Y., Liu, Q. and Li, F. (2023) First Insights into 6PPD-Quinone Formation from 6PPD Photodegradation in Water Environment. *Journal of Hazardous Materials*, **459**, Article ID: 132127. https://doi.org/10.1016/j.jhazmat.2023.132127

[22] Hua, X., Feng, X., Liang, G., Chao, J. and Wang, D. (2023) Long-Term Exposure to 6-PPD Quinone Reduces Reproductive Capacity by Enhancing Germline Apoptosis Associated with Activation of both DNA Damage and Cell Corpse Engulfment in *Caenorhabditis elegans*. *Journal of Hazardous Materials*, **454**, Article ID: 131495. https://doi.org/10.1016/j.jhazmat.2023.131495

[23] Wang, Y., Fu, R., Sun, P., Li, X. and Zhao, W. (2023) Screening Eco-Friendliness Tire Antioxidants Alternatives: Functional 2,2,4-Trimethyl-1,2-Dihydroquinoline Derivatives Design and Toxicity Evaluation. *Environmental Science and Pollution Research*, **30**, 92282-92294. https://doi.org/10.1007/s11356-023-28836-8

[24] Matsumoto, M., Yamaguchi, M., Yoshida, Y., Senuma, M., Takashima, H., Kawamura, T. and Hirose, A. (2013) An Antioxidant, N,N-Diphenyl-P-Phenylenediamine (DPPD), Affects Labor and Delivery in Rats: A 28-Day Repeated Dose Test and Reproduction/Developmental Toxicity Test. *Food and Chemical Toxicology*, **56**, 290-296. https://doi.org/10.1016/j.fct.2013.02.029

[25] https://www.eopugetsound.org/magazine/is/history-and-chemistry-tires

[26] Błaszczyk, A., Augustyniak, A. and Skolimowski, J. (2013) Ethoxyquin: An Antioxidant Used in Animal Feed. *International Journal of Food Science*, **2013**, Article ID: 585931. https://doi.org/10.1155/2013/585931

[27] Masek, A., Chrzescijanska, E., Zaborski, M. and Piotrowska, M. (2014) Dodecyl Gallate as a Pro-Ecological Antioxidant for Food Packing Materials. *Comptes Rendus Chimie*, **17**, 1116-1127. https://doi.org/10.1016/j.crci.2014.03.001

[28] Gunckel, S., Santander, P., Cordano, G., Ferreira, J., Munoz, S., Nunez-Vergara, L.J. and Squella, J.A. (1998) Antioxidant Activity of Gallates: An Electrochemical Study in Aqueous Media. *Chemico-Biological Interactions*, **114**, 45-59. https://doi.org/10.1016/S0009-2797(98)00041-6

[29] Pauls, K.P. and Thompson, J.E. (1982) Effects of Cytokinins and Antioxidants on the Susceptibility of Membranes to Ozone Damage. *Plant and Cell Physiology*, **23**, 821-832.

[30] Saving Coho Salmon: Alternatives for 6PPD in Tire Manufacturing. https://bcgc.berkeley.edu/sites/default/files/01_-_6ppd_finalpresentation.pdf

[31] Hansch, C., Rockwell, S.D., Jow, P.Y., Leo, A. and Steller, E.E. (1977) Substituent Constants for Correlation Analysis. *Journal of Medicinal Chemistry*, **20**, 304-306. https://doi.org/10.1021/jm00212a024

[32] Fabre, H., Hussam-Eddine, N. and Mandrou, B. (1984) Stability-Indicating Assay for Phenylbutazone: High-Performance Liquid Chromatographic Determination of Hydrazobenzene and Azobenzene in Degraded Aqueous Phenylbutazone Solutions. *Journal of Pharmaceutical Sciences*, **73**, 1706-1709. https://doi.org/10.1002/jps.2600731211

[33] Li, J.-J. (2011) Isolation of Lignin from Wood. Bachelor's Thesis, Saimaa University of Applied Science, Imatra.

[34] Anastasiou, E., Lorentz, K.O., Stein, G.J. and Mitchell, P.D. (2014) Prehistoric Schistosomiasis Parasite Found in the Middle East. *The Lancet Infectious Diseases*, **14**, 553-554. https://doi.org/10.1016/S1473-3099(14)70794-7

[35] Gunasekara, H.D.A. (2017) Effect of Lignin Base Antioxidant on Natural Rubber Base Solid Tyre Tread Compound. Doctoral Dissertation, University of Moratuwa, Moratuwa. http://dl.lib.mrt.ac.lk/handle/123/12906

[36] Gellerstedt, G. (2015) Softwood Kraft Lignin: Raw Material for the Future. *Industrial Crops and Products*, **77**, 845-854. https://doi.org/10.1016/j.indcrop.2015.09.040

[37] Sarkanen, K.V. and Ludwig, C.H. (1971) Lignins: Occurrence, Formation, Structure and Reactions.

[38] Mohamad Aini, N.A., Othman, N., Hussin, M.H., Sahakaro, K. and Hayeemasae, N. (2020) Lignin as Alternative Reinforcing Filler in the Rubber Industry: A Review. *Frontiers in Materials*, **6**, Article No. 329. https://doi.org/10.3389/fmats.2019.00329

[39] Barana, D. (2017) Lignin-Based Elastomeric Composites for Sustainable Tyre Technology. https://hdl.handle.net/10281/153251

[40] Carpenedo, G.A., Guerra, N.B., Giovanela, M., Paoli, M.A.D. and Crespo, J.D.S. (2022) Evaluation of Lignin as Stabilizer in Vulcanized Natural Rubber Formulations. *Polímeros*, **32**, e2022036. https://doi.org/10.1590/0104-1428.20220077

[41] Gregorová, A., Košíková, B. and Moravčík, R. (2006) Stabilization Effect of Lignin in Natural Rubber. *Polymer Degradation and Stability*, **91**, 229-233. https://doi.org/10.1016/j.polymdegradstab.2005.05.009