## **Alternative Analysis Report**

Report Date: 2024.03.29

Report To: Department of Toxic Substances Control (DTSC)

Report Subject: Alternative Analysis Report in Response to the Requirements of the US 6PPD Legislation

Dear DTSC: We submit this Alternative Analysis (AA) report on hazardous substances in response to your department's request to ban 6PPD (6propylbenzimidazolone) in the United States. We are committed to environmental protection and public safety, and strongly support your department's efforts to ensure that our products comply with California's safety and environmental standards.

## I. Background

There are various types and wide applications of rubber products, such as construction, transportation, aerospace, national defense and military industry, energy extraction, electronic and electrical, medical and health, daily consumer goods, etc. During the use of rubber products, it is inevitable that they will age due to external factors. Therefore, it is necessary to add an appropriate amount of additives in the rubber processing process to delay the aging process and extend the service life. Among them, the additives used to prevent rubber aging are called rubber anti-aging agents. As one of the main varieties of rubber additives, the global consumption of rubber antioxidants is about 600000 tons/year, accounting for about 40% of the total consumption of rubber additives. According to statistics from the China Rubber Industry Association, the total production of rubber antioxidants in China is 360000 to 420000 tons/year. According to their chemical structure, amine antioxidants can be divided into amine antioxidants, phenolic antioxidants, and other antioxidants. Among them, amine antioxidants can also be subdivided into para phenylenediamine, quinoline, diphenylamine, naphthylamine, and other antioxidants. Currently, the three most widely used antioxidant products in the market are N - (1,3-dimethylbutyl) - N '- phenylpara phenylenediamine (6PPD), 2,2,4-trimethyl-1,2-dihydroquinoline polymer (TMQ), and N-isopropyl-N' - phenylpara phenylenediamine (IPPD), with an annual dosage of about 200000 tons of 6PPD.

In the rubber processing process, sufficient anti-aging agents are added to ensure the aging protection performance of the rubber material. However, when the concentration of anti-aging agents is too saturated, it will migrate from the inside of the rubber to the surface due to the concentration gradient, causing defects on the rubber surface, also known as frost spraying. The frost spraying phenomenon of small molecule rubber anti-aging agents is more prominent. In addition, rubber products also have the problem of aging agent migration during use. The waste and particles generated during the natural aging process of rubber accumulate in the atmosphere and water environment, and the aging agent in the waste and particles will migrate to the environment. At the same time, amine and phenolic rubber aging agents are prone to physical and chemical changes due to their structural characteristics, forming toxic and harmful substances that cause environmental pollution. Therefore, solving the problem of easy migration of rubber anti-aging agents and actively developing green new anti-aging agent products to replace aniline anti-aging agents are inevitable trends for future development. At present, the main products of rubber anti-aging agents in China include anti-aging agents 6PPD, TMQ, and IPPD. Among them, antiaging agent 6PPD has the highest usage due to its excellent comprehensive performance and relatively economic cost advantage. However, there are still many occasions where it is not suitable to use, such as the obvious swelling phenomenon of chloroether rubber Hydran T6000 in petroleum environments, which makes anti-aging agent 6PPD easy to migrate out and not suitable for use. Due to the high safety risks associated with the structure of naphthylamine, some naphthylamine antioxidants, such as antioxidant A, have been phased out and banned. However, there are still a few improved naphthylamine antioxidants applied to nonrubber products, such as the antioxidant phenyl-2naphthylamine in high-density polyethylene plastic pipes, which hardly migrates in distilled water and has little effect on temperature. With the increasing awareness of environmental protection, the green and

environmentally friendly nature of antioxidants has become increasingly important. The "salmon" incident caused by the oxidation of antioxidant 6PPD to form highly toxic substance 6PPD quinone after its migration has attracted widespread attention. Therefore, inhibiting the migration of anti-aging agents is of great significance for the anti-aging, performance, and environmental protection of materials. The preparation of anti-aging agents using natural substances has good development prospects. Lignin anti-aging agent LIGFLEX601-75 is used to replace anti-aging agent TMQ and 6PPD in the composite of butadiene styrene rubber (SBR). The rubber material has a higher crosslinking density and excellent aging resistance, and the mechanical properties of the two rubber materials are basically equivalent. The nonpolluting anti-aging agent DMQ from Shanghai Rebo New Materials Technology Co., Ltd. can replace products such as antioxidants SP-P, BHT, and anti-aging agents TMQ, BLE, etc. It has the same thermal oxygen protection effect and has no impact on the processing performance and physical mechanical properties of NR/BR/SBR rubber. Despite having a certain amount of anti-aging products with excellent migration resistance and anti-aging properties, it is still not possible to completely replace the three universal anti-aging agents (6PPD, TMQ, and IPPD) in the short term.

6PPD (N-phenyl-N '- (1,3-dimethylbutyl) benzodiazole) is a rubber antiaging agent with good heat resistance, oxygen resistance, ozone resistance, and bending resistance. Its chemical structure contains two benzene rings and one diazole ring, which gives 6PPD strong antioxidant properties and good rubber compatibility. Antioxidant 6PPD is widely used in various rubber products such as tires, tapes, hoses, wires and cables, and rubber products. Adding an appropriate amount of 6PPD to rubber products can effectively prevent rubber aging and extend the service life of the products. In addition, 6PPD can also improve the heat resistance, oxygen resistance, ozone resistance, and bending resistance of rubber products, thereby improving the overall performance of the products.

6PPD is very important in the rubber industry. Firstly, it can improve the aging resistance of rubber products. Rubber products are easily affected by various factors such as oxygen, ozone, heat, light, and mechanical stress during use, resulting in a decrease in their performance and a shortened service life. As an efficient rubber antioxidant, antioxidant 6PPD can effectively improve the anti-aging performance of rubber products and extend their service life. Secondly, improve the heat resistance of rubber products. With the continuous expansion of the application field of rubber products is also increasing. Antioxidant 6PPD has good heat resistance, which can improve the heat resistance of rubber products.

Thirdly, it can improve the bending resistance of rubber products. Rubber products are subjected to repeated bending and compression during use, resulting in a decrease in their performance. Antioxidant 6PPD can improve the bending resistance of rubber products, thereby enhancing their durability and service life. Finally, it can improve the processing performance of rubber products. Antioxidant 6PPD has good rubber compatibility, which can improve the processing performance of rubber products, reduce production costs, and improve production efficiency. 6PPD, as an efficient rubber anti-aging agent, has broad application prospects in the rubber industry. Its excellent heat resistance, oxygen resistance, ozone resistance and bending resistance make rubber products have better aging resistance and longer service life in the use process. Rubber tires are essential across various sectors, including transportation and agriculture. Indeed, tire manufacturers produced 19 million tons of rubber in 2019, and continued global industrialization is expected to increase tire demand, requiring nearly 23 million tons annually by 2024. Max-imization of the longevity of tires is a form of sustainability, reducing the annual flow of tires to landfills and other waste streams. This and other pressures have led the development of highly effective rubber additives that protect rubber from degradation during manufacture and use, most notably pphenylenediamines (PPDs). Among these, 6PPD (N-(1,3- dimethylbutyl)-N'-phenyl-p-phenylenediamine) in particular has

gained ubiquity in the tire industry and is included at 0.5–1.5 wt % in standard formulations. As a result, annual U.S. consumption of 6PPD ranges from 50 to 100 million tons, the majority of which is used in tires. Despite widespread use, PPD additives are known to aggravate various toxicity end points for both human and environmental health. 6PPD in particular has recently gained notoriety due to the extreme aquatic toxicity of its quinone transformation product (6PPDQ) to coho salmon and other aquatic species.

In U.S. Pacific Northwest coho salmon (Oncorhynchus kisutch), stormwater exposure annually causes unexplained acute mortality when adult salmon migrate to urban creeks to reproduce. By investigating this phenomenon, we identified a highly toxic quinone transformation product of N-(1,3-dimethylbutyl)-N'- phenyl-p-phenylenediamine) (6PPD), a globally ubiquitous tire rubber antioxidant. Retrospective analysis of representative roadway runoff and stormwater-impacted creeks of the U.S. West Coast indicated widespread occurrence of 6PPD-quinone (<0.3-19 µg/L) at toxic concentrations (LCso of  $0.8 \pm 0.16$  µg/L). These results reveal unanticipated risks of 6PPD antioxidants to an aquatic species and imply toxicological relevance for dissipated tire rubber residues.By searching a recent EPA crumb rubber report for related formulas (i.e., CisHo-xN2-4Oo-y), several characteristics of the C18H24N2 antiozonant "6PPD" [N-(1,3-dimethylbutyl)-N'-phenyl-pphenylenediamine] matched necessary attributes. First, 6PPD is globally ubiquitous (0.4-2% by mass) in passenger and commercial vehicle tire formulations.

These data implicate 6PPD-quinone as the primary causal toxicant for decades of stormwater-linked coho salmon acute mortality observations. While minor contributions from other constituents in these complex mixtures are possible, 6PPD-quinone was both necessary (i.e., consistently present in and absent from toxic and non-toxic fractions, respectively), when purified or synthesized as a pure chemical exposure, sufficient to produce URMS at environmental concentrations. Over the product life cycle, antioxidants (e.g., PPDs, TMQs, phenolics) are designed to diffuse to tire rubber surfaces, rapidly scavenge ground-level atmospheric ozone and other reactive oxidant species, and form protective films to prevent ozone-mediated oxidation of structurally significant rubber elastomers. Accordingly, all 6PPD added to tire rubbers is designed to react, intentionally forming 6PPD-quinone and related transformation products that are subsequently transported through the environment. This antiozonant application of 6PPD inadvertently, yet drastically, increases roadway runoff toxicity and environmental risk by forming the more toxic and mobile 6PPD-quinone transformation product. Based on the ubiquitous use and substantial mass fraction (0.4-2%) of 6PPD in tire rubbers and the representative detections across the

U.S. West Coast, which include many detections near or above LCso values, we believe that 6PPD-quinone may be present broadly in periurban stormwater and roadway runoff at toxicologically relevant concentrations for sensitive species, such as coho salmon.

Globally,  $\sim 3.1$  billion tires are produced annually for our >1.4 billion vehicles, resulting in an average 0.81 kg/capita annual emission of tire rubber particles. TWPs are one of the most significant microplastics sources to freshwaters; 2-45% of total tire particle loads enter receiving waters and freshwater sediment contains up to 5800 mg/kg TWP. Supporting recent concerns about microplastics, 6PPD-quinone provides a compelling mechanistic link between environmental microplastic pollution and associated chemical toxicity risk. While numerous uncertainties exist regarding the occurrence, fate, and transport of 6PPDquinone, these data indicate that aqueous and sediment environmental TWP residues can be toxicologically relevant and existing TWP loading, leaching, and toxicity assessments in environmental systems are clearly incomplete. Tire rubber disposal also represents a major global materials problem and potential potent source of 6PPD-quinone and other tirederived transformation products. In particular, scrap tires re-purposed as crumb rubber in artificial turf fields suggest both human and ecological exposures to these chemicals. Accordingly, the human health effects of such exposures merit evaluation.

Environmental discharge of 6PPD-quinone is particularly relevant for the many receiving waters proximate to busy roadways. It is unlikely that coho salmon are uniquely sensitive, and the toxicology of 6PPD transformation products in other aquatic species should be assessed. For example, used tires were more toxic to rainbow trout (4- fold lower 96hours LCso) relative to new tires, an observation consistent with adverse outcomes mediated by trans- formation products. If management of 6PPD-quinone discharges is needed to protect coho salmon or other aquatic organisms, adaptive regulatory and treatment strategies along with source control and "green chemistry" substitutions (i.e., identifying demonstrably non-toxic and environmentally benign replacement antioxidants can be considered. More broadly, we recommend more careful toxicological assessment for transformation products of all high production volume commercial chemicals subject to pervasive environmental discharge.

Though unknown for decades, 6PPDQ is produced in nearly 10% molar yield upon ozonation of 6PPD. While work is ongoing, this process is believed to occur at the surface of tires and tread wear particles before 6PPD, 6PPDQ, and other trans-formation products enter water systems through roadway runoff in storms.

However, replacement of 6PPD poses a formidable challenge as rubber compounds are susceptible to attack from numerous reactive species peroxyl radicals, alkyl radicals, ozone and 6PPD protects rubber compounds from each of these degradation pathways. Broadly speaking, it is believed that 6PPD protects tires in two distinct but overlapping ways: kinetic scavenging that consumes O3 at the tire surface before it is able to react with the rubber and subsequent formation of a protective film that provides a mechanical barrier against O3.

6PPD is considered an efficient, multifunctional, and low-toxicity product in the rubber industry. It demonstrates good protective effects against ozone and flexing aging in both natural and synthetic rubbers. Additionally, it provides adequate protection against general aging factors such as oxygen and heat, as well as harmful metals like copper and manganese. 6PPD does not easily migrate or volatilize in rubber and its products, and it is resistant to water extraction, making it also used as a stabilizer in synthetic rubber. Due to its excellent protective properties, it is widely used in aircraft, automobile, and bicycle tires, tape industry, cable industry, and waterproofing projects, among other rubber products.

So 6PPD has been used as an anti-depressant for decades and is used in most motor vehicle tires. The key role of 6PPD is to protect the rubber from reacting with ozone and oxygen, so as not to crack. However, 6PPD is toxic to many aquatic organisms throughout the food chain and can affect the survival of wildlife. 6ppd-Quinone is a reaction product of 6PPD that kills fish within hours of exposure. While little is known about the effects of

6PPD-quinone on other organisms, 6PPD-quinone is acutely toxic to salmon found in California. Over the life of the tire, 6PPD migrates to the tire surface, providing protection against degradation due to ozone and oxygen. Tire wear particles (TWP) are produced when a tire rolls on the road, especially when a vehicle brakes, accelerates, and turns. Tire wear particles and the 6PPD can enter the aquatic environment through road dust carried by surface runoff and rainwater. While it's unclear exactly where and how 6PPD-quinone formed, the detection of 6PPD-quinone in California waterways clearly indicates that the chemical is persistent enough in aquatic systems that aquatic organisms are exposed to concentrations at levels that could pose a hazard to it. The concentrations of 6PPD-quinone measured in streams in California were higher than those shown in laboratory experiments. In accordance with the criteria in the SCP Regulations, we determined that aquatic organisms may be exposed to 6PPD and 6PPD-Quinone extracted from motor vehicle tires. This exposure could cause or exacerbate significant adverse effects on aquatic life, including two fresh populations in California, one of which is endangered and the other of which is endangered.

Based on the above situation, we try our best to understand the policies and regulations of DTSC:

(1) The background of the economic and fiscal impact proposed by the California Toxic Substances Administration (DTSC) in April 2022 to

amend California laws and regulations, Title 22, Section 69511.

② On July 26, 2023, the California Toxic Substances Administration (DTSC) passed a regulation.

③On October 1, 2023, tires containing 6PPD will be included in the priority general product list and officially implemented.

(4) On October 1, 2023, tires containing 6PPD will be included in the priority general product list and officially implemented.

(5) In November 2023, the American Tire Manufacturers Association (USTMA) announced its collaboration with the United States Geological Survey (USGS) to evaluate and refine methods for evaluating potential alternatives to 6PPD. At the end of March 2024, the American Tire Manufacturers Association (USTMA) will release the toxicological results of potential alternatives.

<sup>(6)</sup>Submit AA report to California DTSC before March 29, 2024.



DTSC has determined that tires produced by automotive tire manufacturers contain 6PPD, which may be affected by the proposed regulations. DTSC estimates that the cost for California manufacturers to meet DTSC regulatory requirements may range from \$451840 to \$1219840. This economic impact assessment is based on the assumption that motor vehicle tire manufacturers containing 6PPD will fully comply with DTSC regulations and submit priority product notifications and AA reports to DTSC before the dates specified by DTSC, as this is the most conservative financial compliance approach. Car tire manufacturers containing 6PPD may comply with regulations in one of several ways if they do not submit an AA (alternative plan) report:

(1)Remove 6PPD from the tire;

② Replace 6PPD with different chemicals that meet the regulatory requirements of these products;

③ Stop selling tires containing 6PPD in California.

If the manufacturer fails to comply with the regulations, DTSC provides a notice of non-compliance, and importers, retailers, or assemblers should be required to stop the commercial flow of products into California, and retailers and assemblers should stop ordering products.

If manufacturers of priority products cannot be identified or contacted in a reasonable manner, DTSC will track the supply chain to identify responsible entities in the next layer of business. Other responsible entities may include importers, assemblers, or retailers arranged in descending order of responsibility. Generally speaking, AA is a two-stage process that considers many aspects of product manufacturing, including process

engineering, environmental management, financial analysis, and research and development. AA also examined other product features, such as usage and end-of-life management. In the first stage of the AA process, manufacturers need to determine the legal, functional, and performance requirements of priority products and chemicals of concern, and use this information to determine a range of alternative solutions to consider. After the first stage is completed, the manufacturer will record the investigation results in the preliminary AA report and submit this report to DTSC.

In the second stage of the AA process, manufacturers use more in-depth analysis to compare priority products with possible alternatives and consider other factors, including lifecycle and economic impact. This information has been submitted to DTSC in the final AA report.

In response to the above facts, we understand that the United States has made important progress in restricting the use of 6PPD. Under the Washington Safer Products Act, the state of Washington passed Bill 5931 on March 8, 2024, which requires a comprehensive review and regulation of all motor vehicle tires containing 6PPD. In addition, the U.S. Environmental Protection Agency (EPA) is also actively taking action, initiating a risk management process for 6PPD under the Toxic Substances Control Act (TSCA) and working with the American Tire Manufacturers Association (USTMA) on alternatives to 6PPD. EPA also plans to finalize a rule under Section 8 (d) of TSCA that would require manufacturers of 6PPDs to report inventories and copies of unpublished health and safety studies to EPA by the end of 2024.

In addition, the EPA granted petitions from the Yurok, Port Gamble S'Klallam and Puyallup tribes to consider regulations that would prohibit the manufacture, processing, use and distribution of 6PPD in tires. The tribes based their petition on guidelines to protect human health and the environment, particularly in light of 6PPD's negative effects on salmon.

In California, the Department of Toxic Substances Control (DTSC) finalized a regulation under the Safer Consumer Products (SCP) Statute to add motor vehicle tires containing 6PPD to the priority product list. This means that manufacturers need to submit product notices and may need to find alternatives. These measures reflect U.S. concerns about the environmental impact of 6PPD and a commitment to develop and adopt alternatives. The US 6PPD legislation aims to restrict the use of 6PPD in motor vehicle tires to protect the environment, particularly aquatic life. As required by the legislation, tire manufacturers are obligated to conduct an alternative analysis to evaluate the safety and environmental friendliness of potential substitutes.

Doublestar was founded in 1921, headquartered in Qingdao, China, which are China's tire intelligent manufacturing leader. Our goal of PCR is to create the first brand of safety tires, and the goal of TBR is to create the first brand of special tires and become a professional service provider. As a responsible enterprise, we attach great importance to this issue and immediately initiated the analysis of hazardous substance substitution. Although we do not sell tires in California currently, but our factory in Cambodia will start production this year, and we plan to sell our products to California in the future and provide tire service in California. So we have worked closely with relevant experts and partners to comprehensively evaluate the application areas, functions, and potential risks of 6PPD, and actively seek safer alternatives. Fortunately, some progress has been made in the replacement of new products. However, the new product is still in the patent protection, temporarily can not be detailed to the public. But the progress could be share.

II. Alternative Analysis

1. Selection of Alternatives

Through market research and technical studies, we have identified several potential substitutes:

(1) Alternative chemical SA6000: temporarily named SA6000. Through the joint research and development with our upstream partners, we found that SA6000 is equivalent to 6PPD in performance. Specific performance is attached below:

(1)In the water toxicity test of SA6000, before and after ozone aging, no fish died in 100% saturated solution;

(2) For the anti-kinetic, static ozone and anti-thermal oxygen

effects,SA6000 are close to that of 6PPD;

(3) The effect of SA6000 on the dynamic properties of the compound is basically the same as 6PPD;

(4) The effect of SA6000 on the properties of the compound is not significantly different from 6PPD, and it is not necessary to adjust the formula when the same amount is substituted..

After laboratory testing and field trials, we believe that replacing chemical substance A can completely replace 6PPD with minimal impact on human health and the environment.

(2) Research on existing antioxidant products including 6QDI、IPPD、
77PD、CCPD、7PPD、TMQ、NBC、Ethoxyquinoline、DLTP.
①6QDI is structurally almost identical to 6PPD, but it is an oxidized form of 6PPD and we expect it to have similar dangers;



②IPPD is structurally very similar to 6PPD, but it has three more carbon molecules than 6PPD, making it a slightly larger molecule. Because of this size difference, toxicity is slightly less than 6PPD.



③77PD is similar to 6PPD, but unlike 6PPD, it has a limited effect on reproductive toxicity. It is not known whether 77PD forms a substance similar to 6ppd-quinone in the environment, or whether this compound is acutely toxic to salmon.

Chemical (CASRN)	Carcinogenicity	Genotoxicity/Mutagenicity	Reproductive Toxicity	Developmental Toxicity	Endocrine Activity	Acute Toxicity	Systemic Toxicity (single)	Systemic Toxicity (repeat)	Neurotoxicity (single)	Neurotoxicity (repeat)	Skin Sensitization	Respiratory Sensitization	Skin Irritation	Eye Irritation	Acute Aquatic Toxicity	Chronic Aquatic Toxicity	Persistence	Bioaccumulation	Reactivity	Flammability	Benchmark Score
77PD 3081-14-9	L	L	L	М	DG	М	L	М	L	DG	H	М	L	L	vH	vН	H	М	L	L	BM-2

(4) CCPD score is BM1 because of its high persistence, high bioaccumulation, very high acute and chronic aquatic toxicity, very high skin irritation, and high systemic toxicity. It is unclear whether CCPD forms a substance similar to 6ppD-quinone in the environment, or whether this compound is acutely toxic to salmon.



⑤7PPD was BM1 due to high reproductive toxicity. Basically similar to

6PPD, biological accumulation is lower than 6PPD. It is not known whether 7PPD forms quinones in the environment with similar acute toxicity to 6ppd-quinones, and there is no data on salmon toxicity.

Chemical (CASRN)	Carcinogenicity	Genotoxicity/Mutagenicity	Reproductive Toxicity	Developmental Toxicity	Endocrine Activity	Acute Toxicity	Systemic Toxicity (single)	Systemic Toxicity (repeat)	Neurotoxicity (single)	Neurotoxicity (repeat)	Skin Sensitization	<b>Respiratory Sensitization</b>	Skin Irritation	Eye Irritation	Acute Aquatic Toxicity	Chronic Aquatic Toxicity	Persistence	Bioaccumulation	Reactivity	Flammability	Benchmark Score
7PPD 3081-01-4	L	L	н	M	М	L	L	М	L	DG	н	М	L	М	хH	vН	Н	L	L	L	BM-1

(6) TMQ has a high score for acute and chronic aquatic toxicity, although the credibility of the score is low due to the use of weak substitutes and modeling. TMQ is not a PPD type molecule, so it should not form quinones similar to 6PPD quinones in the environment. There is no data on the toxicity of silver salmon.

Chemical (CASRN)	Carcinogenicity	Genotoxicity/Mutagenicity	Reproductive Toxicity	Developmental Toxicity	Endocrine Activity	Acute Toxicity	Systemic Toxicity (single)	Systemic Toxicity (repeat)	Neurotoxicity (single)	Neurotoxicity (repeat)	Skin Sensitization	Respiratory Sensitization	Skin Irritation	Eye Irritation	Acute Aquatic Toxicity	Chronic Aquatic Toxicity	Persistence	Bioaccumulation	Reactivity	Flammability	Benchmark Score
TMQ 147-47-7	м	L	М	М	DG	М	vН	н	DG	DG	L	L	L	L	H	H	H	vL	L	L	BM-2

(7)NBC has a high carcinogenicity because multiple authoritative nickel compounds are carcinogenic. However, due to an 18 month study showing negative carcinogenicity results in mice, the credibility of this endpoint score is low. The toxin service company did not find that the 18 month study was sufficient to overturn the authoritative list, as the two-year study was the standard for carcinogenicity investigation.



(a) Ethoxyquinoline is not as toxic to aquatic organisms as 6PPD, although it is still rated as a high hazard of acute and aquatic toxicity. Ethoxyquinoline is not PPD like many other evaluated compounds, so it does not form conversion products similar to 6PPD quinone

Chemical (CASRN)	Carcinogenicity	Genotoxicity/Mutagenicity	<b>Reproductive Toxicity</b>	<b>Developmental Toxicity</b>	Endocrine Activity	Acute Toxicity	Systemic Toxicity (single)	Systemic Toxicity (repeat)	Neurotoxicity (single)	Neurotoxicity (repeat)	Skin Sensitization	<b>Respiratory Sensitization</b>	Skin Irritation	Eye Irritation	Acute Aquatic Toxicity	Chronic Aquatic Toxicity	Persistence	Bioaccumulation	Reactivity	Flammability	Benchmark Score
Ethoxyquin 91-53-2	L	L	М	М	М	М	vН	н	DG	DG	М	DG	L	L	H	H	H	vL	L	L	BM-2

(DLTP has low toxicity to freshwater organisms (fish, invertebrates, and algae), and its hazard assessment is rated as low risk of acute and chronic aquatic toxicity. DLTP is not a PPD type molecule and therefore cannot form substances similar to 6PPD quinone in the environment. There is no data on the toxicity of silver salmon or its toxicity to other salmon species. But it belongs to the category of plastic assisted antioxidants.



The above product analysis leads to the following conclusions:

(1) The above several antioxidants in addition to 6PPD have sufficient data to show that under the action of sunlight and ultraviolet light, 6PPD quinone is formed, which has a fatal effect on the silver salmon during the spawning period. Several other PPD antioxidants do not have sufficient data to show that they produce 6PPD quinones.

(2) If further studies confirm that 6ppd-quinone is responsible for cosilver salmon mortality before spawning, other PPD compounds could serve as acceptable alternatives to reduce negative impacts on coho until safer alternatives are developed. However, given the anti-ozone properties of other PPD molecules, they are not an ideal long-term solution for the anti-ozone activity of tires.

(3)On the above chemicals evaluated, all got the BM1 (Chemicals of high concern) except the 77PD. Therefore, 77PD May also be a suitable replacement for 6PPD, as it is also a member of the PPD class of chemicals. However, reviews from pre-USTMA suggest that it will not provide durable enough protection for tires and may need to be combined with other chemicals. Further research is therefore needed to determine if there are situations or combinations where these chemicals may have acceptable anti-ozone oxidizer properties compared to 6PPD.

(4) There may be other chemical alternatives that we haven't looked at. There are also some examples of tires in use that can be used without the addition of 6PPD as an anti-ozone agent, where the chemical used for this purpose has not been disclosed. Because 6PPD is a UV resistant compound, tires that are not exposed to UV light may not contain 6PPD. These include tires for indoor forklifts, etc. In addition, there are examples of white tires that comply with all road legal regulations, which may also not contain 6PPD because it will change the color of the tires. Airless tires (i.e., nonpneumatic tires) are currently being developed that will use less or no rubber, as only the tread may contain rubber - and the sidewalls will not. Airless tires are not yet available for passenger cars, but in other applications such as golf carts, special work vehicles and forklifts. Manufacturers are working on products for passenger cars.

(3) Improving production process: We have considered improving the production process to reduce the usage of 6PPD. After technical evaluation, we found that improving the production process can reduce the use of 6PPD, but it cannot completely replace 6PPD.

(1)Optimized formulation: By adjusting the concentration of 6PPD and using other auxiliary additives to reduce its decomposition in the rubber, thus reducing the generation of toxic substances.

(2)Improve the polymerization process: Optimize the rubber manufacturing process, including polymerization, vulcanization and other steps to reduce the decomposition of 6PPD during production and use.

③Improved tire design : By improving the design of tires to reduce tire

and road friction and wear, thereby reducing 6PPD and its breakdown products into the environment.

(4) Implement an Environmental Management system: Implement an environmental management system during production and disposal to monitor and control the use and emissions of 6PPD.

(5) Improve industry standards and regulations: Drive the shift to more environmentally friendly production processes across the industry by developing more stringent industry standards and regulations.

It is important to note that the implementation of these approaches requires industry collaboration, technological innovation, and policy support. At the same time, any improvement measures should undergo a rigorous environmental and health risk assessment to ensure their effectiveness and safety.

(4) Other types of rubber additives: Such as anti-ozone agents, anti-aging agents, anti-fatigue agents, etc. However, the development of new rubber additives needs to follow the principles of environmental protection, sustainability and safety.

①Research on regulations and standards:

Study in detail the content of the US 6PPD Act to understand its restrictions and requirements on the use of 6PPD (N-phenyl-N '- (1,3-dimethylbutyl) benzodiazole) in rubber additives. Understand other relevant regulations, such as the EU REACH regulation and California Proposition 65, to ensure the compliance of new rubber additives in the global market.

(2) Principles of Green Chemistry:

In the development process of adhesive additives, green chemistry principles are adopted, such as using harmless raw materials, designing efficient synthesis routes, and reducing waste generation. Priority should be given to bio based and biodegradable chemicals to reduce their impact on the environment.

③Toxicological assessment:

Comprehensive toxicological evaluation of rubber additives, including acute toxicity, chronic toxicity, genetic toxicity, carcinogenicity, reproductive toxicity, and developmental toxicity. Evaluate the potential toxicity of additives through in vitro experiments and animal models.

(4) Performance testing:

Test the physical and chemical properties of new rubber additives on a laboratory scale, such as oxidation resistance, ozone resistance, fatigue resistance, etc. Conduct rubber formula experiments to evaluate the impact of additives on rubber processing performance and final product performance.

(5) Security assessment:

Environmental impact assessment, including biodegradability, soil and water resource pollution risks, etc. Evaluate the safety of additives during use, disposal, and recycling processes. **(6)**Life Cycle Assessment (LCA):

Rubber additives undergo a lifecycle assessment, analyzing the entire process from raw material collection, production, use to waste disposal, to assess their impact on the environment and human health.

⑦Collaboration and Certification:

Collaborate with certification agencies to obtain environmental and safety certifications, such as Blue Angel and Green Seal. Collaborate with rubber manufacturers to conduct industrial scale application testing.

(a)Marketing and Education:

Develop a marketing plan to promote the safety and performance advantages of new rubber additives to potential users. Provide technical support and training to help users use new rubber additives correctly.

⑨Continuous improvement:

Provide feedback and market information to continuously improve the performance and safety of rubber additives. Follow up the latest scientific research and technological development to ensure the progressiveness and competitiveness of rubber additives.

Through the above steps, a new type of rubber additive that meets the requirements of the US 6PPD Act can be developed, while ensuring its superior performance and minimizing its impact on the environment and human health, thereby promoting the sustainable development of the rubber industry.

## 2. Evaluation of Alternatives

We have conducted a comprehensive evaluation of the potential substitutes, taking into account safety, environmental impact, cost, performance, and other aspects.

(1) Safety: The substitutes can pass relevant safety tests and meet the safety standards set by the DTSC.

(2) Environmental Impact: The substitutes have a minimal impact on the environment during production, use, and disposal. Some substitutes are biodegradable, which is beneficial for environmental protection.

(3) Cost: The cost of the substitutes is comparable to 6PPD, and some substitutes being less expensive, offering certain economic advantages.

(4) Performance: The substitutes are equivalent to 6PPD in enhancing the tire ozone resistance, and even some perform even better.

**III.** Conclusion and Recommendations

Based on comprehensive analysis, we believe that SA6000 can meets the requirements in terms of performance, safety, and environmental friendliness, and can effectively reduce risks to human health and the environment, so SA6000 can be used as a substitute for 6PPD. Meanwhile, we will continue to focus on the research progress of alternative chemical B and consider improving production processes when conditions are ripe. To ensure that our products meet the requirements of California DTSC, we will continue to maintain close communication with relevant departments

and actively cooperate with regulatory work. We promise to strictly comply with California environmental regulations and effectively protect human health and environmental safety during the implementation of new alternative solutions.

Finally, we would like to express our gratitude to California DTSC for their attention and support in our work, and we look forward to your department's review and guidance on our report. We will continue to work hard to contribute to the sustainable development of California.

Best Regards!

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