Bisphenol A Alternatives in Thermal Paper

Executive Summary

FINAL REPORT

August 2015 [Supercedes version dated January 2014]

U.S. Environmental Protection Agency

Executive Summary

This report provides information on bisphenol A (BPA), its use in thermal paper, and possible substitutes for this use. The report was developed by the U.S. Environmental Protection Agency (EPA) with input from stakeholders from business, government, academia, and environmental organizations. Based on conversations with technical experts, including stakeholders, we identified nineteen alternatives that are potential functional substitutes for inclusion and assessment. In addition to information on potential hazards of BPA and possible substitutes, information on the trade-offs associated with each alternative is presented for consideration in substitution decision-making.

Background

In March 2010, EPA released a chemical action plan for BPA. BPA is a high production volume (HPV) chemical that is used in manufacturing most polycarbonate plastics, the majority of epoxy resins, and other uses subject to regulation under the Toxic Substances Control Act. The action plan summarizes hazard, exposure, and use information, and identifies actions to address BPA in the environment based on concerns for potential effects on aquatic species.¹ BPA is also a commonly used developer in a number of thermal paper applications, such as point-of-sale (POS) receipts. The developer is a component of a chemically reactive layer of thermal paper, which reacts in the presence of heat to create the printed image. When used in thermal paper, BPA is present as "free" (i.e., discrete, non-polymerized) BPA, which is likely to be more available for exposure than BPA polymerized into a resin or plastic (U.S. EPA 2010).

One component of the action plan tasked the EPA Design for the Environment (DfE) Branch to conduct an alternatives assessment for BPA in thermal paper. Thermal paper was selected for evaluation based on concern for potential exposures to consumers and workers, releases to the environment, and stakeholder interest. DfE's Alternatives Assessment Program provides a basis for informed decision-making by developing a semi-quantitative, screening-level comparison of the potential human health and environmental impacts of chemical alternatives. DfE Alternatives Assessments provide information on functional use class, intrinsic hazard, exposure properties, and environmental fate for chemical alternatives. Information from DfE Alternatives Assessments can support the selection of safer alternatives when combined with other information not addressed in DfE Alternatives Assessments, such as performance, cost, and life-cycle impacts.

Goal of the Alternatives Assessment and Report Overview

In July 2010, DfE convened a multi-stakeholder effort to assess the human health and environmental effects of BPA and its alternatives as developers in thermal paper. This informal partnership includes a diverse array of stakeholders, such as thermal paper manufacturers, thermal paper converters, chemical manufacturers, POS equipment manufacturers, retailers, trade associations, non-governmental organizations (NGOs), green chemistry and technical experts, and international governmental organizations. The outcome of this effort is presented in this report. The report provides information that will help decision-makers consider

¹ The U.S. Food and Drug Administration (FDA) is expected to take the lead on assessing potential human health impacts associated with exposure to BPA. See <u>www.fda.gov/ForConsumers/ConsumerUpdates/ucm297954.htm</u>.

environmental and human health profiles for all evaluated chemicals so that they can choose safer functional alternatives and take into account potential hazard trade-offs that may exist.

Chapter 1 of this report provides background information on BPA and defines the report's purpose and scope. Chapter 2 discusses information on BPA and its use in thermal paper as a developer. Chapter 3 offers background information on the thermal paper printing system and how developers interact with other components in the system to create a printed product. Chapter 4 explains the hazard evaluation methodology and includes the hazard profiles for BPA and the alternatives. Chapter 5 provides exposure information and life-cycle considerations for BPA. Chapter 6 discusses considerations for selecting thermal paper developers and provides relevant resources for moving towards a substitution decision.

Hazard Evaluation of BPA and Alternatives

Given that the project scope is limited to BPA's use as a developer in thermal paper, this alternatives assessment does not consider alternatives to BPA for other uses. In addition to BPA, 19 potential chemical alternatives were identified for evaluation, which were considered by stakeholders likely to be functional in thermal paper. The assessment evaluated three general attributes to inform decision-making on chemical alternatives: (1) human health effects, (2) ecotoxicity, and (3) environmental fate. The evaluation was conducted according to the *DfE Alternatives Assessment Criteria for Hazard Evaluation*, which is a transparent tool for evaluating and differentiating among chemicals based on their human health and environmental hazards. For most endpoints, the criteria define "High," "Moderate," and "Low" concern. Very few chemicals had measured data for all endpoints; therefore, estimation methods were applied to fill data gaps. Since estimation methods come with a lower degree of confidence, this circumstance may be an important consideration for decision-making. No clearly safer alternatives to BPA were identified in this report – most alternatives have Moderate or High hazard designations for human health or aquatic toxicity endpoints. Persistence and bioaccumulation potential were not distinguishing for this group of alternatives.

The human health effects endpoints evaluated in DfE Alternatives Assessments include acute toxicity, carcinogenicity, genotoxicity, reproductive toxicity, developmental toxicity, neurotoxicity, repeated dose toxicity, skin sensitization, respiratory sensitization, eye irritation, and dermal irritation. Qualitative discussions on available endocrine activity and immunotoxicity data were included, where relevant. All chemicals (including BPA) had Low designations for acute mammalian toxicity. Eight chemicals had High designations for developmental toxicity. For repeated dose toxicity, five chemicals had a High designation. Thirteen chemicals had Moderate, High, or Very High designations for at least one of the irritation and sensitization endpoints. All chemicals were assigned Moderate concern for carcinogenicity. Six chemicals were assigned Moderate concern for this endpoint.

The ecotoxicity endpoints evaluated in DfE Alternatives Assessments include acute and chronic aquatic toxicity. Ecotoxicity data for terrestrial species is limited. Most of the alternatives had High designations for aquatic toxicity (acute and chronic).

Environmental fate of BPA and the 19 alternatives were also evaluated. Three of the 20 chemicals had Low or Very Low persistence values; 11 had High or Very High persistence values. Only two chemicals had a High bioaccumulation potential.

For a screening-level summary of the hazard evaluations for alternatives (including BPA), see Table ES-1 below.

General Exposure and Life-Cycle Factors

Environmental exposure to BPA or alternatives may occur during manufacture, conversion, or use of thermal paper, at its end-of-life (i.e., recycling, landfilling, or incineration), or during manufacture of recycled paper products. Understanding the factors that affect exposure to BPA and alternative developers across their life-cycles provides additional context to the alternative selection process. There is a potential for occupational exposure during chemical and product manufacturing and product end-of-life. Additionally, there may be exposures to workers and consumers while thermal paper is being used and to the general population and the environment from releases during product manufacturing, use, and end-of-life.

Considerations for Selecting Thermal Paper Developers

Along with presenting information on hazard to inform substitution decisions, the report discusses considerations for selecting thermal paper developers, including opportunities for innovation and design challenges. Options that may be considered for substitution include the development of new chemicals that have a preferable hazard profile while still meeting the performance considerations required by particular applications. Another option would be to re-design thermal paper to eliminate the need for chemical developers. In addition to reconfiguring thermal printing systems, decision-makers may wish to consider alternative printing systems. These systems should be evaluated and compared to thermal printing to better understand relative performance, cost, and hazard. Finally, another option would be the use of ereceipts. A full examination of the relative merits of thermal paper versus e-receipts would require the consideration of life-cycle impacts, which is beyond the scope of this study.

How to Use This Report

The intended audience for the report includes, but is not limited to, chemical manufacturers, product manufacturers, retailers, consumers, NGOs, consultants, and state and federal regulators. Four possible uses of this report include: (1) identification of potential substitutes, (2) selection of alternative chemicals based on comparative hazard assessment, (3) incorporation of hazard information for further analysis and decision-making, and (4) as a baseline for the development of new and safer chemical substitutes.

This report allows stakeholders interested in chemical substitution to identify functional substitutes for BPA in thermal paper. The list of potential alternatives introduced in Chapter 3 includes chemicals identified by stakeholders as likely to be viable, functional alternatives as well as chemicals that are not considered functional alternatives, which were subsequently removed from consideration. The inclusion of a chemical in this assessment does not indicate environmental- or health-based preferability. By identifying potential functional alternatives, this report assists manufacturers in selecting chemicals for additional performance testing.

Chapter 4 contains human health and environmental profiles for each chemical. Decision-makers can use this information to understand and compare the hazard concerns associated with potential alternatives, and it may help businesses avoid the cost of repeated substitution. Some

alternatives may be associated with hazard concerns similar to those of BPA, while others may be associated with different hazard concerns. The profiles in Chapter 4 can help decision-makers understand which potential alternatives may come under scrutiny in the future.

In addition to reading the hazard summary table (ES-1), decision-makers should review the full hazard assessments for each chemical available in Section 4.2 of the report. The hazard assessments provide more information on hazard criteria, data interpretation, and information used to assign hazard values in each category. Decision-makers should consider this information to ensure a complete understanding of the hazard profiles of each alternative.

The information in this report can be used to inform further analyses on preferred alternative chemicals, such as risk assessments or life-cycle assessments. For example, a decision-maker could identify several preferred functional alternatives and conduct product-specific risk assessments based on exposure expectations along the product's life-cycle. This type of supplementary information may be helpful in guiding product-specific decision-making. The criteria used to develop the hazard assessments in this report can also be used to inform green chemistry design, if availability of safer alternatives is limited.

Many of the chemicals have significant data gaps; while estimation methods can be used to address these data gaps, access to high quality, relevant toxicological and environmental fate data is preferred as it provides more robust assessments. Chemicals used at high volumes, or likely to be used at high volumes in the future, should be of high priority for further testing. The full hazard assessments for each chemical, available in Chapter 4, may inform whether additional assessment or testing is needed.

ES-1 Screening Level Toxicology Hazard Summary for BPA and Alternatives

This table only contains information regarding the inherent hazards of the chemicals evaluated. Evaluation of risk considers both the hazard and exposure. The caveats listed in the legend and footnote sections must be taken into account when interpreting the hazard information in the table below.

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from estimation software and professional iudgment. [§] Based on analogy to experimental data for a structurally similar compound. Aquatic Environmental **Human Health Effects** Toxicity Fate **Skin Sensitization Dermal Irritation** Bioaccumulation Carcinogenicity Developmental **Repeated Dose** Acute Toxicity **Eye Irritation** Reproductive **Respiratory** Sensitization Neurological Genotoxicity Persistence Chemical Chronic (for TSCA inventory name and Acute relevant trade names see the individual profiles in Section 4.8) CASRN Structure **Bisphenol A and Phenolic Alternatives** но-Bisphenol A 80-05-7 Μ Μ Μ L Μ L Μ Η М Μ Η H VL L 2,2-bis(p-hydroxyphenyl)propane Bisphenol F 'nΩ M[§] H^{δ} M§ 620-92-8 М Η VH Η L М L L Μ L L Bis(4-hydroxyphenyl)methane Bisphenol C L§ **M** § M§ M§ 2,2'-Bis(4-hydroxy-3-79-97-0 Μ H§ М M§ H§ Μ M Η Η M methylphenyl)propane MBHA $L^{\$}$ L§ M[§] H§ M§ M§ M§ 5129-00-0 М Η М L Η М L Methyl bis(4-hydroxyphenyl)acetate **BisOPP-A** 24038-68-L§ L§ M[§] M§ M§ M§ M[§] 4,4'-Isopropyllidenebis(2-H§ M М Η Η M L 4 phenylphenol) **Bisphenol** AP H^{\S} 1571-75-1 L§ L§ M[§] M§ M^{\S} M§ M§ Η М М Η Η М 4,4'-(1-Phenylethylidene)bisphenol Substituted phenolic compound, $L^{\$}$ M[§] H§ M§ M§ M§ M§ М L М Η М L М **PROPRIETARY #1** Substituted phenolic compound, L§ M[§] M§ M§ M§ M§ L§ H§ М М Η Η Η Η **PROPRIETARY #2** PHBB 94-18-8 **M**[§] ∣ L§ М L VL L М М L М VL Η Η L Benzyl 4-hydroxybenzoate

ES-1 Screening Level Toxicology Hazard Summary for BPA and Alternatives (Continued) This table only contains information regarding the inherent hazards of the chemicals evaluated. Evaluation of risk considers both the hazard and exposure. The caveats listed in the legend and footnote sections must be taken into account when interpreting the hazard information in the table below.

VL = Very Lo were assigned	w hazard $L = Low hazard M = N$ based on empirical data. Endpoints i	Aoderate hazaı n black italics	d <mark>H</mark> (VL, L	= High , <i>M, H</i> ,	hazar	d VH =	= Very	High	hazar	'd —	Endpoi	nts in	colored				
y Dubbu on un			Aquatic Enviro											onmental Fate			
Structure	Chemical (for TSCA inventory name and relevant trade names see the individual profiles in Section 4.8)	CASRN	Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
но он	Bisphenol S 4-Hydroxyphenyl sulfone	80-09-1	Hydro L	oxyphe M	nyl Sulf M	fone A	lternat M	ives M	Н	L		L	L	M	M	Μ	L
HO CH CH	2,4-BPS 2,4'-Bis(hydroxyphenyl)sulfone	5397-34-2	L§	М	M	M§	M [§]	М	H [§]	L§		L§	L§	М	H	М	L
но-С-Он	TGSA Bis-(3-allyl-4-hydroxyphenyl) sulfone	41481-66-7	L	М	L	M§	M§	М	Н	Μ	М	L	VL	Н	Μ	Н	L
	BPS-MAE Phenol,4-[[4-(2-propen-1- yloxy)phenyl]sulfonyl]-	97042-18-7	L	M§	M	M§	M§	М	L	L	М	L	VL	н	н	Н	L
	BPS-MPE 4-Hydroxy-4'- benzyloxydiphenylsulfone	63134-33-8	L	М	M§	M§	M§	М	H§	L		L	L	VH	H	Н	М
	D-8 4-Hydroxyphenyl 4-isoprooxyphenylsulfone	95235-30-6	L	М	L	M§	M§	М	M	L§		L§	L§	Н	H	Μ	Μ

ES-1 Screening Level Toxicology Hazard Summary for BPA and Alternatives (Continued)

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 \ddagger The highest hazard designation of any of the oligomers with MW <1,000

§ Based on analogy to experimental data for a structurally similar compound.

			Human Health Effects										Aquatic Toxicity		Environmental Fate		
Structure	Chemical (for TSCA inventory name and relevant trade names see the individual profiles in Section 4.8)	CASRN	Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Oligomeric and Polymeric Alternatives																	
᠆ᡐᡃᡉ᠋ᢩᠯᠬ᠋ᡐᡝᡐᡃ	D-90 Phenol, 4,4'-sulfonylbis-, polymer with 1,1'-oxybis[2-chloroethane]	191680-83-8	L	М	L	L	L	М	L	L		Μ	VL	L [‡]	L^{\ddagger}	VH [‡]	H^{\ddagger}
"O~~~O"	DD-70 1,7-bis(4-Hydroxyphenylthio)-3,5- dioxaheptane	93589-69-6	L	М	L	М	M§	М	M§	M§		H§	M§	H	Н	Н	L
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Pergafast 201 N-(p-Toluenesulfonyl)-N'-(3-p- toluenesulfonyloxyphenyl)urea	232938-43-1	L	М	L	M	M	L	M	L		L	VL	Н	Н	VH	L
arusaira	BTUM 4,4'-bis( <i>N</i> -carbamoyl-4- methylbenzenesulfomide)diphenylme thane	151882-81-4	L	М	L	L	L	L	Μ	L		L	L	Н	Н	Н	L
	UU Urea Urethane Compound	321860-75-7	L	М	L	L	L	L	L	L		L	L	L	L [◊]	VH	L