Regulatory and Sustainability Initiatives Lead to Improved Polyaminopolyamide-epichlorohydrin (PAE) Wet Strength Resins and Paper Products

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ABSTRACT

Polyaminopolyamide-epichlorohydrin (PAE) resins are the predominant commercial products used to manufacture wet strengthened paper products. Since their development in the late 1950s, the first generation (G1) resins have proven to be one of the most cost effective technologies available to provide wet strength to paper. Throughout the last three decades, regulatory directives and sustainability initiatives from various organizations have driven the development of "cleaner" and safer PAE resins and paper products.

Early efforts in this area focused on improving worker safety and reducing the impact of PAE resins on the environment. These efforts led to the development of resins containing significantly reduced levels of 1,3-dichloro-2-propanol (1,3-DCP) and 3-monochloropropane-1,2-diol (3-MCPD), potentially carcinogenic by-products formed during the manufacturing process of PAE resins. As the levels of these by-products decreased, the environmental, health and safety (EH&S) profile of PAE resins and paper products improved. Today, initiatives from major retailers in the United States are focusing on product ingredient transparency and quality, thus encouraging the development of safer product formulations that maintain the original functional performance characteristics.

In Europe, the predominant technology is second generation (G2) resins. G2 resins contain less than 1,000 parts per million of 1,3-DCP on an "as received" basis. These resins provide sufficient wet strength to paper but with lower efficiency (higher cost) compared to G1 technology.

PAE resin research over the last fifteen years has been directed toward regulatory requirements to improve consumer safety and to minimize exposure to potentially carcinogenic materials found in various paper products. One of the best known regulatory requirements is the recommendations of the BfR (the German Federal Institute for Risk Assessment), which defines the levels of 1,3-DCP and 3-MCPD that can be extracted by water from various food contact grades of paper. These criteria led to the development of third generation (G3) products that contain very low levels of 1,3-DCP (typically less than 10 parts per million in the "as received" resin).

This paper outlines the PAE resin chemical contributors to AOX and 3-MCPD in paper and provides recommendations for the use of each PAE resin product generation (G1, G1.5, G2, G2.5 and G3).

Keywords: Polyaminopolyamide-epichlorohydrin resin, PAE resin, wet-strength, polymer-bound, AOX, 3-MCPD, regulatory, sustainability, BfR, ANVISA.

INTRODUCTION

Polyaminopolyamide-epichlorohydrin (PAE) resins are the predominant chemistry used to wet strengthen a diverse range of paper industry products. First developed and marketed in 1957 [1], the early PAE resins quickly displaced urea-formaldehyde (UF) technology for wet strengthening tissue and towel products. Today, they are also used to provide wet strength to grades such as liquid packaging board (for milk and juice), board (beverage carriers), tea bag and coffee filter paper and specialty grades such as currency. These paper products are designed to retain a portion of their dry strength, typically 20 to 35%, under aqueous conditions to fulfill the consumer need.

Following the initial development of PAE resins sixty years ago, resin manufacturers continued to conduct research and to innovate. The innovation focus has been on development of products with (1) an improved environmental, health and safety (EH&S) profile and (2) higher solids to reduce freight costs. Although products containing higher solids typically were less efficient, G1 products recently closed that gap [2]. The effort to improve the EH&S profile resulted in less efficient and more expensive PAE resin products. Innovative concepts and advances in process chemistry and engineering improved the cost efficiency of G2 products and closed the efficiency gap between G2 and G3 product offerings.

In the past thirty years, greater awareness of the hazards posed to human health and the environment by some of the processes and chemicals used to manufacture paper products has resulted in various regulatory measures being imposed on the industry. To ensure business sustainability, papermakers must comply with these regulatory measures typically through operational changes. In addition, these same regulatory concerns have motivated chemical suppliers to develop new products and technologies to help papermakers meet these ever-changing demands.

As these regulatory measures evolved, newer generations of PAE resins were developed. Typically, these regulatory measures are specific to a region; therefore, the development of a global solution will not meet the current manufacturer and consumer needs in all regions. However, paper manufacturers who produce for the global market must ensure that regulatory compliance for both grade and region are met [3].

In addition to the external regulatory measures imposed on the industry, major producers of wet-strengthened paper products maintain corporate sustainability programs to ensure the long-term viability of their businesses. These programs often include a commitment to environmental sustainability by reducing the impact of their overall manufacturing footprint.

PAE resin manufacturers have focused their product improvement and development efforts on the paper manufacturers' improved health and sustainability objectives. These objectives varied widely due to market and regional differences. Regulatory directives are the main catalyst for "cleaner" products with much lower levels of epichlorohydrin (epi) by-products and adsorbable organic halides (AOX). Additionally, higher solids and higher efficiency PAE resins positively influence sustainability. The types of sustainability directives and initiatives that need to be considered are summarized in Table I.

Table I – Types of Sustainability Directives and Initiatives

Governmental Regulations	NGO Guidelines	Cost and Performance
Worker safety [e.g., Globally Harmonized System (GHS) SDS's, OSHA, California Proposition 65, Volatile Organic Compounds (VOCs)] using PAE resins	Non-Governmental Organizations' guidelines for product and environment (e.g., EU Ecolabel, Blue Angel, Nordic Ecolabel, Green Seal, paper manufacturers and major retailers)	Maximize solids to minimize transportation (reduce freight cost, carbon dioxide and pollutants), "fewer trucks on the road"
Consumer safety (e.g., FDA, BfR, GB 9685, ANVISA) using paper products made with PAE resins		Resin efficiency at time of customer usage. More efficient resin allows lower dosage, higher retention of PAE (less PAE resin in effluent)
Environmental safety (e.g., GHS, EPA, REACH) using PAE resins (AOX in effluent, aquatic toxicity, VOC)		

BACKGROUND

The basic underlying chemistry for the manufacture of a PAE resin has not really changed in nearly sixty years [4]. A low molecular weight polyaminopolyamide, known as a prepolymer, is initially formed by polycondensation of adipic acid and diethylenetriamine (DETA), but alternative dibasic acids (and acid derivatives) and polyalkylenepolyamines have been used (Figure 1). The ratio of the adipic acid and DETA can be varied to provide a prepolymer with higher amine functionality, which provides lower levels of 1,3-dichloropropanol (1,3-DCP) and 3-monochloropropane-1,2-diol (3-MCPD) in the PAE resin [5]. An aqueous mixture of the prepolymer is alkylated with epichlorohydrin (epi) at 20 to 40 °C to initially form tertiary aminochlorohydrin (ACH) functionality. Good temperature control is required to minimize epi hydrolysis and to minimize chloride ion formation [6]. After the initial alkylation step, the reaction mixture is heated to 60 to 80 °C. This step results in further conversion of ACH functionality to azetidinium (AZE) functionality (Figure 2) and further crosslinking to build a PAE resin of the desired molecular weight. The reaction is quenched with acid (typically sulfuric acid) at the target viscosity and cooled to less than 25 °C before pumping to storage.

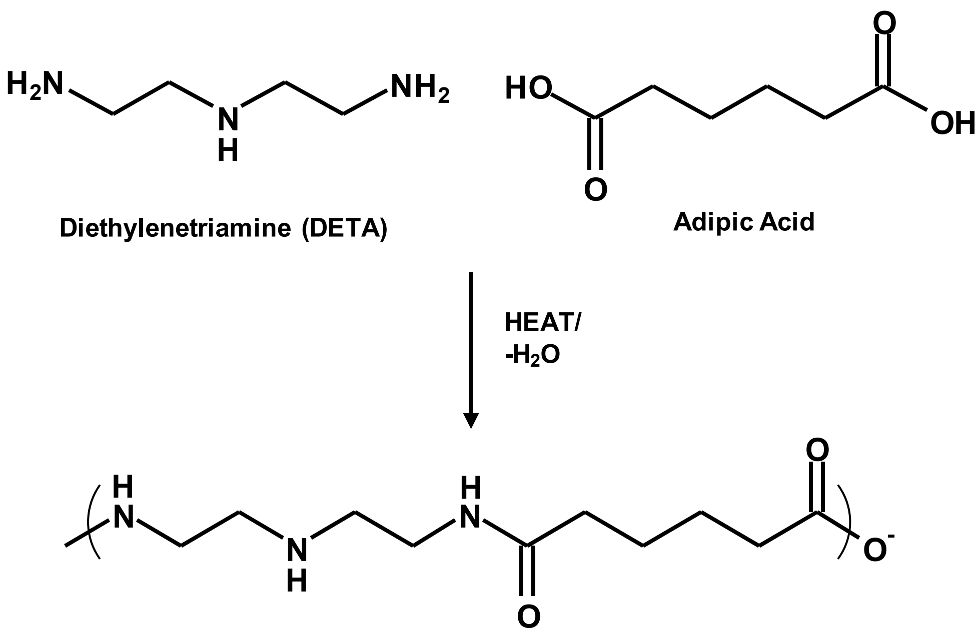

Figure 1 – Typical Manufacture of Polyaminopolyamide Intermediate to PAE Resin.

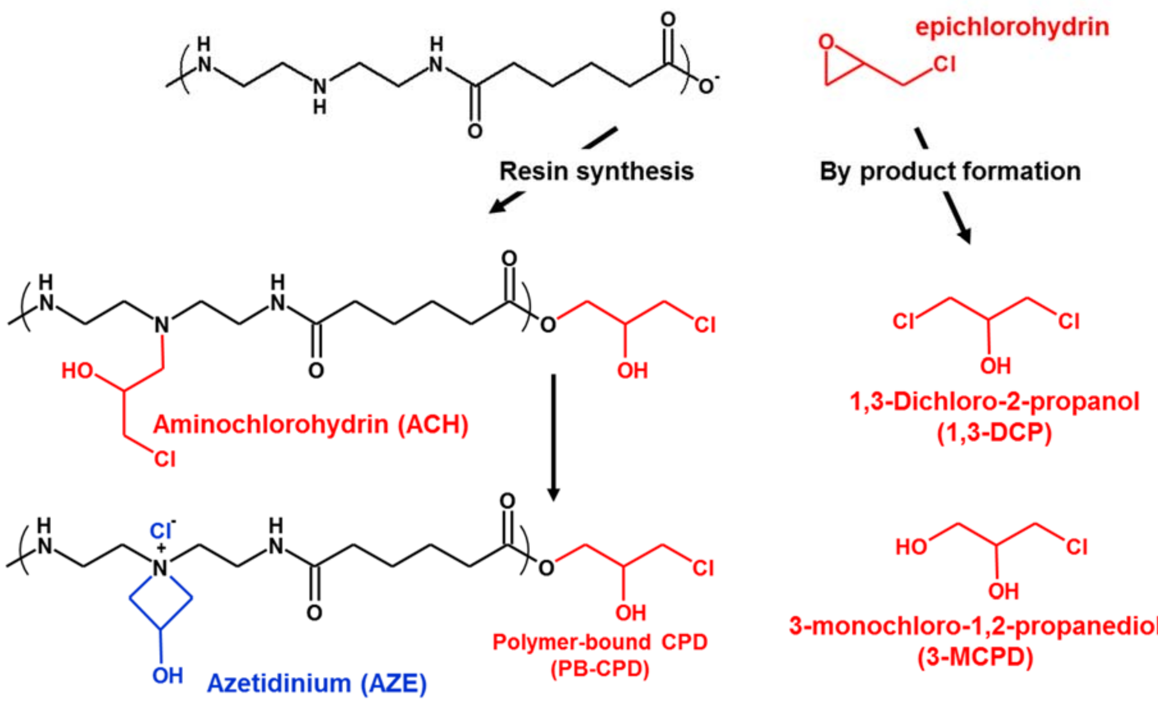

Figure 2 – Typical PAE Resin Manufacture and Formation of Epi By-products.

RESULTS AND DISCUSSION

To confirm compliance with governmental directives and non-governmental organizations' guidelines, the chemistry that affects each directive and guideline must be considered. In PAE wet-strength resins, two types of organic chlorine species exist (Figure 2): (1) free epi by-products (1,3-DCP and 3-MCPD) and epi (typically at very low levels) and (2) polymer bound organic chlorine (PBOX) species: (a) ACH, the principle species formed from the initial reaction between epi and the amine groups of the poly(adipic acid-co-diethylenetriamine) prepolymer and (b) PB-CPD, the species formed from the reaction between epi and the acid end groups of the prepolymer. An additional free epi by-product is 2,3-dichloropropanol (2,3-DCP), which, except for its AOX content, is not regulated. This by-product is typically at very low levels but can be significant when low quality epi is used in the PAE resin manufacturing process.

The free epi by-products and the PBOX species in the PAE resin are inter-related regarding regulations and guidelines, which can result in confusion. In an effort to clarify, the following sections will be presented; (1) global governmental regulatory directives and non-governmental organizations' guidelines, (2) worker safety with PAE resins and epi by-products, (3) consumer safety with paper products treated with PAE resins, (4) environmental effects of PAE resins and AOX and (5) PAE resins' effects on the total organic chlorine content of paper. As PAE resins evolved, the product definitions regarding AOX and epi by-products became inconsistent across product "generations" [7]. These definitions are not arbitrary but are based on key customer needs.

Global Governmental Regulatory Directives and Non-Governmental Organizations' Guidelines

All PAE resins sold as wet-strength resins in the United States (US), including recently commercialized resins, comply with the FDA 21 CFR 176.170. The Food Contact Notification (FCN) process for new Food Contact Substances indicates only one instance (FCN 276) of a new PAE resin chemistry, but this product is not currently available commercially [8]. For the foreseeable future, no new FDA (i.e., no new legal regulatory) requirements are expected in the US.

However, in the decades since FDA approval of PAE resins, several global governmental directives and non-governmental initiatives have affected the levels of 1,3-DCP, 3-MCPD and AOX in PAE resins and in the final paper consumer product. Best known are the recommendations of the BfR, which are relevant to food contact paper products manufactured or sold in the European Union (EU). In the future, other regions likely will implement BfR type regulations. For example, Brazil's ANVISA has implemented new regulations that take effect on June 29, 2018 and are similar to the BfR recommendations [9]. PAE resin manufacturers and paper manufacturers in Brazil are preparing for these upcoming changes.

In addition to governmental regulatory directives, non-governmental organizations (i.e., not legally binding) are globally active and can affect PAE resins. The well-known Nordic Ecolabel and EU Ecolabel guidelines restrict the levels of 1,3-DCP and 3-MCPD in PAE resins. Even in the US, major retailers have announced recent initiatives that could affect the levels of 1,3-DCP and 3-MCPD in food contact packaging [10]. Recently, PAE resin manufacturers and paper manufacturers have addressed the impact of California (CA) Proposition 65. Furthermore, in North America, towel, paper and paperboard manufacturers typically have internal sustainability initiatives to address the levels of 1,3-DCP and 3-MCPD in their products.

In addition, prior to June 1, 2015, PAE resin manufacturers addressed the hazard communication changes mandated by the legal requirement to implement the Globally Harmonized System (GHS). In North America, these changes resulted in some customer concerns with the new hazard statements that have to be addressed. Moreover, a comparison of GHS Safety Data Sheets (SDSs) shows clear differences between manufacturers. For example, some PAE resin products containing greater than 0.1% (1000 ppm) of 3-MCPD indicate Category 1B reproductive toxicity and include the H360 statement "May damage fertility or the unborn child" on the SDS.

PAE Resins, Epi By-Products and Their Impact on Worker Safety (and VOC)

While epichlorohydrin (epi) is used to generate the key reactive functionality (AZE) and structure (molecular weight) for PAE resins, side reactions with epi result in the formation 1,3-DCP and 3-MCPD. The formation of 3-MCPD is the result of hydrolysis of epi. The formation of 1,3-DCP results from the reaction between epi and chloride ion. The chloride ion is generated from the crosslinking reaction and from the formation of AZE species.

One of the concerns of users of PAE resins is the level of 1,3-DCP and 3-MCPD and very low levels of residual epi present in the wet-strength resin. All three substances are considered to be carcinogenic [11]. When first developed, PAE resins had high levels of 1,3-DCP and 3-MCPD (Figure 3). Freshly produced resins have detectable quantities of residual epi. The level of residual epi rapidly decreases to non-detectable levels (less than one part per million) with all modern PAE resins.

As the carcinogenic nature of these organochloride species became understood, European (and similar North American) legislation was introduced that necessitated that containers of PAE resin containing 1,000 ppm or more of 1,3-DCP (in the "as delivered/received" product) would have to be labeled with "May cause cancer." and either a "skull and crossbones" (under older European legislation) or the newer "health hazard" symbol (mandatory after June 1, 2015 in both Europe and the United States). R&D efforts by the major chemical suppliers to reduce the levels of the epi by-products resulted in what are now known as "Generation 2" PAE resins. These resins were developed through a combination of revised formulations and greater process control (to improve the efficiency of functionalizing the polymer with epi). The resulting resins contained less than 1000 ppm of 1,3-DCP in the "as received/delivered" product [6].

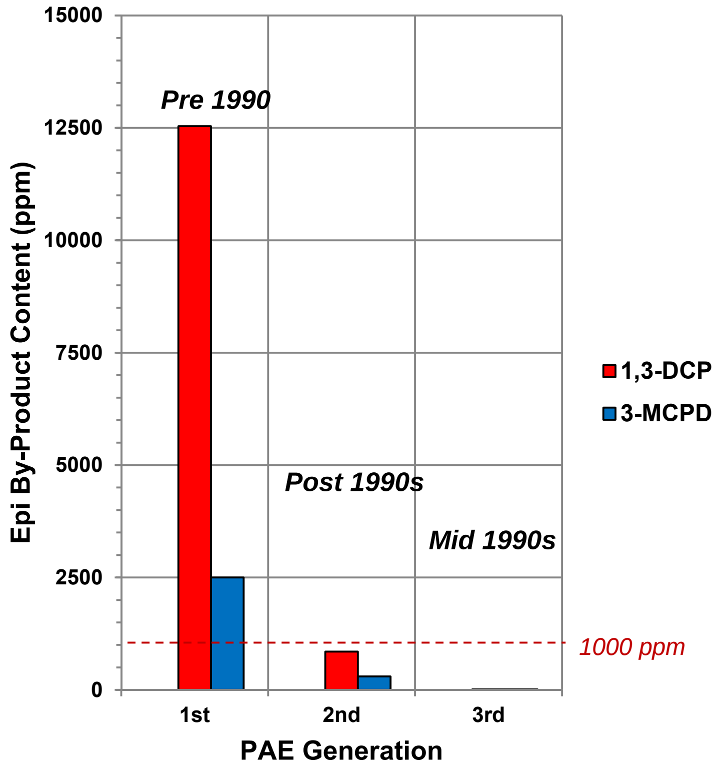

Figure 3 – The Reduction of Epi By-products (12.5% active basis) and the Historical Definitions of G1, G2 and G3 Resins.

With some paper producers looking for resins with levels of epi by-products significantly lower than 1000 ppm, the research and development efforts of suppliers continued. This resulted in a number of post-reaction cleaning techniques that could be applied to Generation 1 or 2 wet strength resins to reduce the level of epi by-products to less than10 ppm in the "as received/delivered" PAE resin products and still provide an acceptable wet strength response. Post-treatment technologies include microbial dehalogenation [12], membrane filtration [13] and carbon absorption [14]. It was discovered that technologies that only removed free 1,3-DCP and free 3-MCPD still contributed to 3-MCPD in paper. The evidence indicated that this 3-MCPD contribution to paper was due to polymer-bound CPD (PB-CPD). This PB-CPD is believed to be due to "CPD-ester" functionality, with the main CPD-ester functionality shown in Figure 2. Both free 3-MCPD and PB-CPD in PAE resins contribute to 3-MCPD in paper. Therefore, processes were developed and commercialized to provide G2.5 and G3 PAE resins with greatly reduced levels of PB-CPD [15]. These processes essentially completely destroy the CPD-ester functionality. A basic ion exchange process can also be used to destroy 1,3-DCP, 3-MCPD, PB-CPD and AOX, but it is costly and produces a significant industrial waste stream [16]. Additionally, an on-site base activation process was developed to remove 1,3-DCP, 3-MCPD, PB-CPD and AOX [17].

For a PAE technology to be classified as G2.5 or G3, it is proposed that the PB-CPD must be reduced to a very low level. The level of PB-CPD can be easily determined by using the so-called “acid test” [15] or more sophisticated analyses. The acid test is relatively simple: the PAE resin is acidified to pH 1.0 with sulfuric acid and held at 50 ^{o}C for 24 hours. The 3-MCPD level of PAE resin before the acid test is subtracted from the 3-MCPD level after the acid test. For G2.5 and G3 resins, the difference is less than 5 ppm, typically less than 1 ppm. For G1-G2.5 resins, the accuracy of the PB-CPD determination is greatly improved by removing free 1,3-DCP and free 3-MCPD to a low level using membrane filtration or other technology on a sample of the PAE resin prior to the acid test.

To further define the Generations of PAE resins, G1 products are those resins that contain more than 1000 parts per million (ppm) of 1,3-DCP in the “as received/delivered” product. The SDS for these products must disclose the presence of 1,3-DCP, and must include a warning regarding the carcinogen hazard of 1,3-DCP. Further, the United States hazard communication legislation requires that the SDS indicate that 1,3-DCP is listed as a potential carcinogen by the International Agency for Research on Cancer. G1 wet-strength resin SDS and labels prepared according to the GHS of Classification and Labeling of Chemicals (mandatory in the Europe and the United States as of June 1, 2015), contains the following Hazard Identifications (Section 2 of the SDS):

GHS-Classification:
Hazardous Classification: Carcinogenicity, Category 1B or 2; Chronic aquatic toxicity, Category 3

GHS-Labeling:

Symbol(s):	(Health Hazard)	
Signal Word:	Danger	
Hazard Statements:	H350	May cause cancer or suspected of causing cancer
	H412	Harmful to aquatic life with long lasting effects

For G2 wet-strength resins, which contain less than 1000 ppm of 1,3-DCP, classification and labeling for carcinogenicity, including the Health Hazard pictogram, is not required. Under the European regulation on Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), 1,3-DCP is considered to be a Substance of Very High Concern (SVHC). As such, wet-strength resins that contain more than 1000 ppm of 1,3-DCP cannot be manufactured or imported into the European Union.

The epi by-products, 1,3-DCP and 3-MCPD, also are potential contributors to the Volatile Organic Compound (VOC) content of the resin. Therefore, the total amount of these species present in the product must be considered for mills and customers that have limitations on VOC levels in their local operating environment.

Certain Eco Labels place limitations on the total sum of 1,3-DCP, 3-MCPD and epi that is present in the wet strength resin. For producers of tissue paper (e.g., kitchen towel) seeking an accreditation from Nordic Ecolabel or EU Ecolabel, the total sum of 1,3-DCP, 3-MCPD and epi in the wet strength resin cannot exceed 7000 ppm (expressed on a dry basis) [18]. This approach, coupled with the limitation of 1,3-DCP on the delivered product for the purposes of SDS and labeling, indirectly defines the amount of 3-MCPD that can be present in the resin. Additional provisions also limit the amount of any residual starting monomer (i.e., adipic acid, DETA and epi) to 100 ppm. In practice, residual epi is at non-detectable levels (less than one ppm) at the time of customer receipt of the PAE resin.

PAE Resins, Epi By-Products in Paper and Consumer Safety
Initial concerns about epi by-products in PAE technology were related to the potential hazard to human health when handling the product and the impact they had on the environment. The focus in recent years has been the potential for these epi by-products to enter the food chain by migration from various food contact grades. After much review and assessment of such risks, the German Federal Institute of Risk Assessment (Bundesinstitut für Risikobewertung, BfR) provides a series of recommendations (XXXVI) for the levels of 1,3-dichloro-2-propanol (1,3-DCP) and 3-monochloro-1,2-propandiol (3-MCPD) that may be extracted with water from a paper sample or product manufactured for different types of food contact grades of paper.

For all food contact paper grades, the recommendation states that the “1,3-dichloro-2-propanol must not be detectable in water extract of the finished product (detection limit 2µg/l). The transfer of 3-monochloro-1,2-propanediol into the water extract of the finished product must be as low as technically achievable, a limit of 12µg/l must not be exceeded in any case.”

While the BfR recommendation for the water extract is the same for all the different types of paper grades, the sample size and the method of aqueous extraction must be considered to appreciate what this means in terms of the levels of the allowable 1,3-DCP and 3-MCPD in paper (Table II).

Table II – Summary of BfR XXXVI Recommendations

Recommended Sample Size and Extraction Method for the Determination of 1,3-DCP and 3-MCPD in Paper Samples							
Sample Type	**Sample Weight**	**Extraction Method**	**Hot/Cold Extraction**	**BfR Limit in Water Extract**		**BfR Limit in Calculated Back to Paper**	
				1,3-DCP	3-MCPD	1,3-DCP	3-MCPD
Teabag/ coffee filter	40g/l (10g/250 mls)	EN647	HOT	2 µg/l	12 µg/l	50 ppb	300 ppb
Kitchen Towel	4g/l (1g/250 mls)	EN645	COLD	2 µg/l	12 µg/l	500 ppb	3000 ppb
Wipes	40g/l (10g/250 mls)	EN645	COLD	2 µg/l	12 µg/l	50 ppb	300 ppb
Other Grades	40g/l (10g/250 mls)	EN645	COLD	2 µg/l	12 µg/l	50 ppb	300 ppb

Considering the sample size and the test methodology, kitchen towel grades are permitted higher levels of 1,3-DCP and 3-MCPD in the final paper product. For all other food contact grades, the levels permitted in the paper are one order of magnitude lower.

While the recommendations originate from Germany, they have been adopted by the different European countries and European Union institutions (for example the 2004 Policy Statement from the Council of Europe concerning Tissue Paper, Kitchen Towels and Napkins). The recommendations apply to food contact grades used in Europe, regardless of whether the paper is manufactured in or imported to the region. Therefore, to be active in the European market, producers worldwide need to ensure that their products comply with these recommendations.

The amount of 1,3-DCP and 3-MCPD in paper manufactured from PAE resins is dependent on a number of papermaking factors including: the amount of 1,3-DCP, 3-MCPD and PB-CPD in the PAE resin; the PAE resin dosage; cycle-up of 1,3-DCP and free 3-MCPD (which is dependent on the water closure level); amount of broke or recycled paper used (especially if the recycled paper used a G1 resin); solids before the dryer section; and drying conditions. In practice, 1,3-DCP and free 3-MCPD are poorly retained by pulp fibers. The amount of 1,3-DCP and free 3-MCPD in the PAE resin is an inaccurate predictor for the amount of 1,3-DCP and 3-MCPD that will be in the paper [e.g., 1 part per million (ppm) of 3-MCPD in the PAE resin is not likely to result in one part per billion (ppb) of 3-MCPD measured in the paper]. Paper testing is needed to ensure compliance.

With current PAE resins, an examination of paper test results reveals that the 3-MCPD levels are much higher than the 1,3-DCP levels even when much more 1,3-DCP is present in the wet strength resin product. Usually, papermakers struggle to meet the limits for the level of 3-MCPD while the 1,3-DCP level is typically well below the

BfR limits. Differences in the partition coefficients with the pulp fibers and the differences in volatility between 1,3-DCP and 3-MCPD are two causes for the higher 3-MCPD level measured in paper.

However, the principle cause of high levels of 3-MCPD found in (and extracted from) paper is the generation of 3-MCPD in the papermaking process. G1 and G2 wet strength resins contain a significant amount of PB-CPD species [produced from the reaction of epi and acid end groups in the prepolymer (Figure 2)]. The PB-CPD species (also known as "CPD-esters") are part of the polymer that is adsorbed and retained by pulp fibers and fines in the wet-end, which are formed into the wet paper web in the wire and press sections of the paper machine (Figure 4). In the dryer section, the action of heat causes hydrolysis of the ester bond; thereby generating an acid end group on the polymer and freed 3-MCPD, both of which remain in the dried paper sheet (Figure 5). During paper testing, the total of the initial free 3-MCPD before the dryer section and the freed 3-MCPD is measured to determine compliance with the recommendations of the BfR.

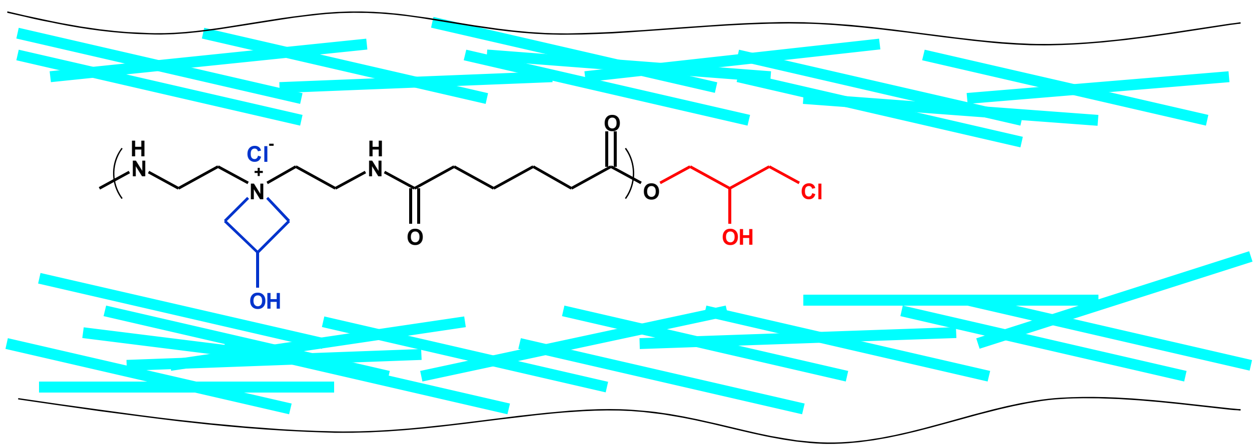

Figure 4 – PAE Resin Polymer Retained on Fiber and Fines in the Wet Web. 1,3-DCP and free 3-MCPD are poorly retained but will cycle-up in the water component of the wet web.

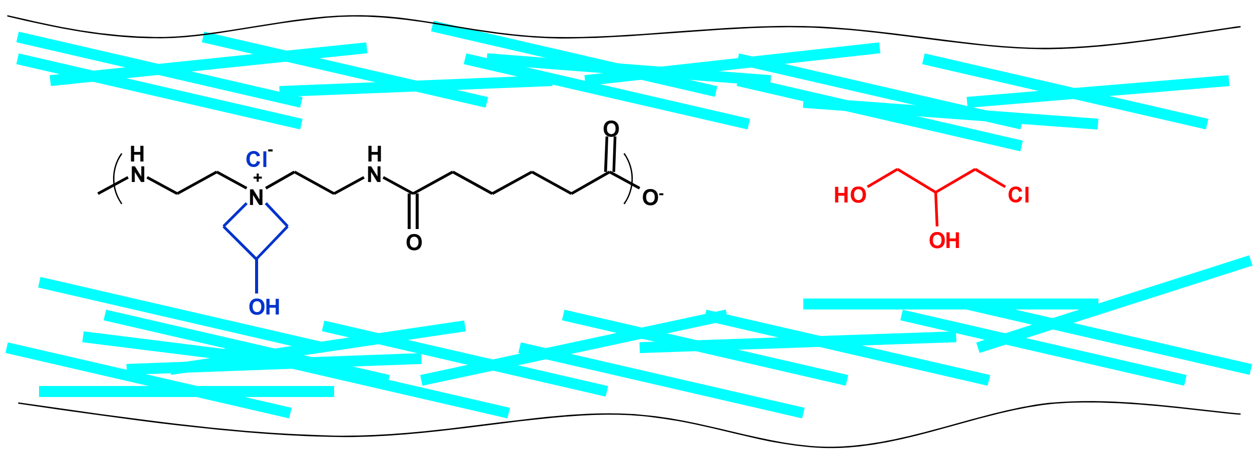

Figure 5 – Hydrolysis of the CPD-ester on PAE Resin Polymer in the Dryer Section. Both the PAE Resin and the Freed 3-MCPD are Retained in the Dry Web and in the Paper Sheet.

In kitchen towel grades, resins that contain small amounts of PB-CPD (e.g., G2 resins) can still allow papermakers to produce products that comply with the BfR XXXVI recommendations due to the lower paper sample size for the BfR test method permitting higher levels of 1,3-DCP and 3-MCPD to be present in the paper. However, for other grades, (such as napkins, tea bag paper, coffee filters and liquid packaging board), the paper sample size used in the test method is higher, thereby resulting in lower limits for 1,3-DCP and 3-MCPD to be present in the paper. PAE resins that contain PB-CPD species may result in levels of 3-MCPD that are not compliant with the BfR XXXVI/1, XXXVI/2 and XXXVI/3 recommendations. A PAE resin with very low or even non-detectable levels of free 3-MCPD could result in a paper with high levels of 3-MCPD if the PAE resin has a significant level of PB-CPD.

Formulation and process conditions for PAE resins can minimize the formation of PB-CPD. However, to achieve the very low levels of PB-CPD needed for G2.5 and G3 resins, post-manufacturing processes are needed. While initial products were based on acidic or enzymatic treatment to hydrolyze PB-CPD, basic treatment is currently the most cost effective process resulting in the highest efficiency PAE resins. The basic treatment destroys much of the 1,3-DCP. During the basic treatment process, most of the initial 1,3-DCP, free 3-MCPD and PB-CPD is ultimately removed from the PAE resin due to further reaction with amine functionality on the polymer and due to further hydrolysis to glycerol. This destruction of 1,3-DCP, free 3-MCPD and PB-CPD reduces the environmental impact and potential hazard to human health when handling these products.

While hydrolysis processes can actually increase the overall free 3-MCPD in the resin, the low substantivity of 3-MCPD to paper fibers (relative to PB-CPD on the cationic polymer) results in an overall lower level of 3-MCPD in the paper product. Additionally, these hydrolysis processes allow post-treatment processes (e.g., microbial dehalogenation or membrane separation) to eliminate the PAE resin contribution to 3-MCPD to paper resulting in a G3 resin. G3 resins have less than 10 ppm of 1,3-DCP and free 3-MCPD but most importantly, exhibit no potential to generate 3-MCPD due to having very low levels of PB-CPD. Use of G3 resins allows papermakers to produce products that meet all the recommendations of the BfR.

PAE Resins Effect on AOX and the Environment

The epi by-products, 1,3-DCP and 3-MCPD are the focus of worker safety and food contact paper regulations. Due to their AOX contribution, 1,3-DCP, 3-MCPD, PB-CPD and ACH in PAE resins also affect environmentally driven regulations and guidelines. Legislation, such as the German Waste Water Act, imposes financial penalties on papermakers based on the level of AOX in their effluent stream. AOX is a blanket term that quantifies the amount of organochloride containing compounds that can be adsorbed onto activated charcoal from water. The term, and methodology used does not distinguish the chemical nature of different organochloride containing species. It is a sum parameter for quantifying the total organic halogen load in water and is often used as a surrogate measure of persistent organic pollutants (POP) in the environment.

The methods for determining AOX have been standardized worldwide. A number of methods exist such as US EPA Method 1650C, DIN EN 1485 and ISO 9562. All of these methods follow the same basic principles: (1) a known quantity of aqueous sample is mixed with activated charcoal, (2) the charcoal is carefully washed with nitric acid to displace and remove any ionic halides (usually chloride ions) from the matrix and (3) the total halide (TOX) content is determined.

In the mid 1980s, a large amount of paper was produced using pulps bleached with chlorine gas. The organochloride compounds present in these pulps were the major contributor to the AOX content of a papermaker's effluent stream. The AOX contribution from the bleaching of pulp has been addressed by the use of alternative bleaching techniques: (1) chlorine dioxide for elemental chlorine free (ECF) bleaching and (2) ozone/hydrogen peroxide for total chlorine free (TCF) bleaching.

After bleaching of papermaking pulps, the next major contributor to the AOX content of a papermaker's effluent stream was PAE resins. The development of Generation 2 wet strength products to address worker safety regulations by reducing the levels of 1,3-DCP and free 3-MCPD also reduced the AOX content. The high levels of 1,3-DCP found in Generation 1 products are a significant contributor to a papermaker's effluent stream.

However, 1,3-DCP and free 3-MCPD are not the only sources of organochloride species that can be determined by the AOX methodology and contribute to a papermaker's effluent stream. Low 1,3-DCP containing resins are sometimes referred to as low AOX. However, with G2, G2.5 and G3 resins, PBOX is by far the primary contributor to AOX, not the free species, 1,3-DCP and free 3-MCPD. In the manufacture of a PAE resin, epi reacts with the secondary amine groups of the prepolymer to form ACH. This ACH species then converts to AZE functionality (Figure 2). Additionally, epi also reacts with the acidic end groups of the prepolymer to generate PB-CPD. Both ACH and PB-CPD are examples of PBOX species. In the AOX methodology, the polymeric component of the PAE resin is retained on the activated charcoal and contributes significantly to the measured AOX.

Theoretically, the AOX content is the sum of the chloride content from the 1,3-DCP, 3-MCPD, PB-CPD and polymeric ACH in the PAE resin. The chloride content of 1,3-DCP is 55 wt % and the chloride content of 3-MCPD is 32 wt %. The contribution of 3-MCPD to the AOX content of a resin is lower than theoretical because 3-MCPD is not completely adsorbed and retained by activated charcoal in the AOX methodology. Whereas 90 to 95% of 1,3-DCP can be retained by activated charcoal, typically only 25% of 3-MCPD is retained under the same conditions. This is due to the greater hydrophilic nature of the 3-MCPD molecule.

The polymeric component of the PAE resin is considered to be well retained by the activated charcoal in the AOX methodology, so an abridged version of the equation (AOX = PBOX + 0.55xDCP) has been found to provide a good description of the AOX content of the PAE. Prior to 1990, Generation 1 PAE resins had high levels of AOX mainly because of the high levels of 1,3-DCP present. The development of Generation 2 wet strength resins, resulted in a reduction not only of 1,3-DCP, by about one order of magnitude, but also in the AOX content of the PAE resin.

An analysis of the relative contributions of the free species (1,3-DCP and 3-MCPD) compared to the PBOX in a G2 PAE resin shows a much higher contribution of PBOX species to the AOX value. This is further exemplified by the application of a post-reaction cleaning technique to a G2 resin to remove only the 1,3-DCP and the 3-MCPD (Figure 6). To emphasize the fact that AOX, 1,3-DCP and 3-MCPD are not necessarily directly correlated and that PBOX is a primary contributor to AOX, note that a G1 resin can be designed to have an AOX level that is higher or lower than the 1,3-DCP level.

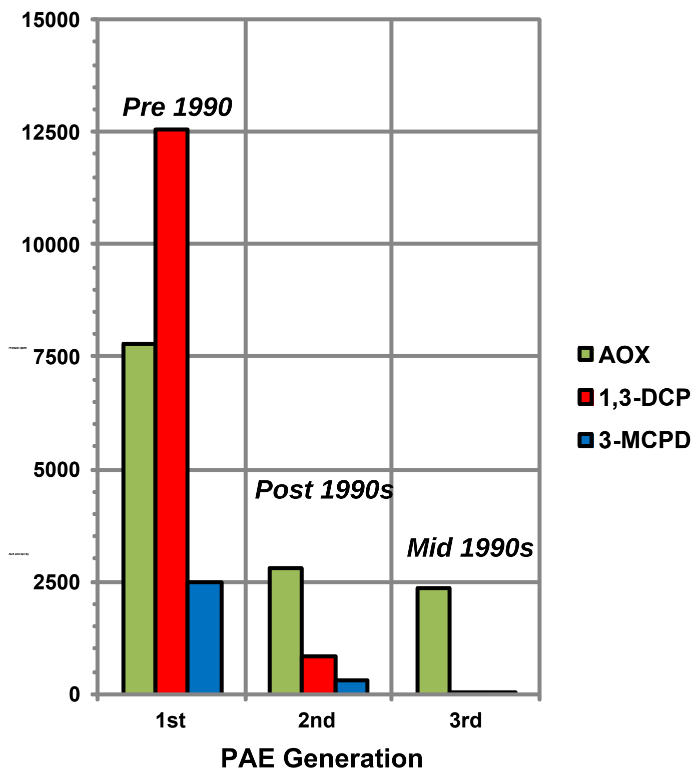

Figure 6 – AOX Content Relative to the 1,3-DCP and 3-MCPD Content (12.5% active basis), Demonstrating the Contribution from PBOX Species (polymeric ACH and PB-CPD).

While the PBOX content decreases from G1 to G2 to G2.5 to G3, the high PBOX content of G2 resins, relative to the 1,3-DCP and the 3-MCPD content, clearly shows that PBOX species are the major contributors to AOX in G2, G2.5 and G3 resins. In practice, most of the polymeric component of the PAE resin is retained in the paper product. This retained PBOX does not contribute to the AOX in a mill's effluent discharge. A high level of retained PAE resin (and therefore a lower AOX in effluent contribution) can be achieved by using best practice application techniques (e.g., optimum dosing points and anionic co-factors).

High efficiency PAE resins with a high AZE level and therefore a high cationic charge are better retained than resins with a low AZE level when best application practices are employed. Additionally, resins with a high AZE level typically have a low level of ACH species, further minimizing the PBOX contribution to AOX. With high efficiency PAE resins, the conversion of ACH to AZE during manufacture is maximized and the conversion of AZE to ACH during aging is minimized resulting in lower PBOX at the time of papermaker use and, therefore, lower AOX in effluent.

In G2 resins, PB-CPD and especially polymeric ACH remain the major source of AOX in PAE resins. With G2.5 and G3 resins, the PBOX content of PAE resins is further reduced by greatly reducing the level of PB-CPD. With G3 resins, polymeric ACH is the only significant contributor to AOX. When considering how much a PAE resin contributes to the AOX content of an effluent stream, papermakers need to consider the actual/total AOX content of the resin and not just the level of epi by-products present in a product.

PAE Resin Effect on Total Organic Chlorine Content of Paper and Consumer Preference
Some manufacturers produce grades of paper considered to be Total Chlorine Free (TCF). For such grades, the Total Organic Halogen (TOX) content is less than 30 mg per kg of dry paper. These grades use TCF pulps, which are produced using oxygen-based bleaching agents (such as ozone and/or hydrogen peroxide). Several methods, such as ISO 11480 and PTS RH12/90, can be used to determine the (total) organic chlorine of pulp and paper. The principles of these methods are similar to those used for the determination of AOX content of aqueous samples, except that the paper sample is mixed with activated charcoal. The measured value is typically called organic halogen (OX) in paper. As with AOX in aqueous samples, the OX in paper is a sum parameter and does not differentiate between the different species present in the paper that contribute to the final value.

As with AOX in aqueous samples, all the organic chlorine species present in the PAE resin contribute to the OX content of the final paper product. The OX content in paper is primarily driven by the PBOX content and not by free epi by-products (1,3-DCP and 3-MCPD) for G2, G2.5 and G3 resins. The following example illustrates this concept:

When considering the maximum limits for epi by-products in paper (kitchen towel):

- 500 ppb of 1,3-DCP equates to 0.28 mg/kg of OX in the paper.
- 3000 ppb of 3-MCPD equates to 0.98 mg/kg of OX in the paper.

Even at the limits recommended by the BfR, free epi by-products are not significant contributors to the OX content of paper. The PBOX species of the resin are the main contributors to the OX content of paper.

Of the two PBOX species present in the resin, polymeric ACH is the principle source of organic chlorine. The proprietary manufacturing processes for G2.5 and G3 wet-strength resins, which were developed to eliminate PB-CPD species from the final product, also reduce the level of ACH, thereby reducing the total AOX and PBOX content of the resin. Therefore, the same G2.5 and G3 resins that allow papermakers to minimize mill effluent AOX content also allow manufacturers to produce TCF grades of paper.

The evolution of cleaner PAE resin technology to help papermakers meet regulatory measures to address environmental and health concerns related to organochloride species has resulted in a better understanding of the PAE resin technology. Improved process control in the basic resin manufacturing process and the development of novel post-reaction techniques were needed to address these concerns. This improved knowledge of PAE resins has been used across all the different generations of PAE technology to generate products with better performance characteristics that can be shipped at higher solids.

Development of a New Class (G1.5) of High Solids, High Efficiency, Wet-Strength Resin Products
Resin products with higher wet strengthening performance and higher solids present minimize the impact on the environment. More efficient PAE resins result in lower PAE resin usage to provide the required level of wet strength for a grade. In addition to the benefit of using less chemistry, the overall presence and contribution of organochloride sources in a papermaking system is reduced. Higher solids versions of PAE resins contribute to a smaller environmental impact in terms of transportation of the resin from the supplier to the papermaker. Fewer

tanker trucks are needed on the road; thus, in addition to a freight cost savings, the overall emissions associated with transporting PAE resins are reduced. These attributes align with the corporate environmental sustainability programs of major papermakers and their customers.

PAE resin manufacturers have focused significant effort to develop higher solids and high efficiency resins. Previously discussed research efforts [2] resulted in a breakthrough in resin design such that resins with 12.5 to 30% solids can be manufactured without compromising performance or gelation stability. Most recently, a new 26% solids, high efficiency, PAE resin was developed with much lower 1,3-DCP, 3-MCPD and VOC than traditional G1 resins. Since the 1,3-DCP level is not low enough to be a G2 resin, this resin is in a new class termed Generation 1.5 (G1.5) due to its much improved EH&S profile. Notably, G1.5 resins have less than 0.1% (1000 ppm) of 3-MCPD and do not indicate Category 1B reproductive toxicity and do not include the H360 statement "May damage fertility or the unborn child" on the SDS. Figure 7 summarizes the attributes of the different Generations of PAE resins.

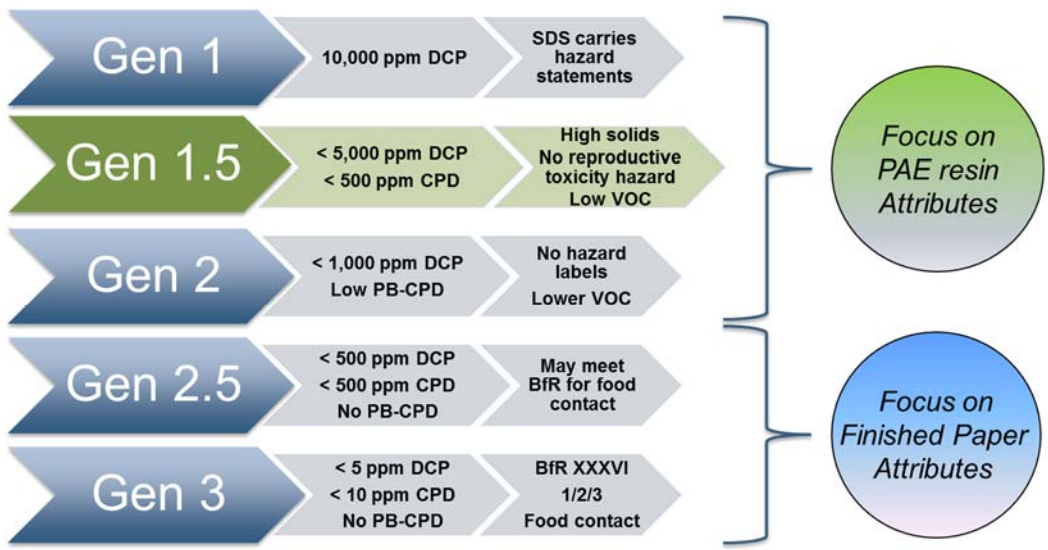

Figure 7 – PAE Resin EH&S Class Summary.

Figure 8 shows 3-MCPD in paper due to the CPD (PB-CPD) difference between a new G2 resin, the new 26% G1.5 resin and a typical competitive G1 resin. The dosage was 1.0% (dry resin on dry fiber), the furnish was 70:30 HW:SW and the papermaking was at pH 7.5. The extraction method was EN645 using 1 gram of paper for 250 mls of water (i.e., the kitchen towel method). In this evaluation and at equal dry dosage, the new G2 resin about half the 3-MCPD in paper relative to the new G1.5 resin and the new G1.5 resin has less than half the 3-MCPD in paper relative to a competitive G1 resin. With this Noble & Wood handsheet evaluation, the pulp furnish is very dilute, thus the free 3-MCPD does not significantly contribute to the 3-MCPD in paper (i.e., the 3-MCPD in paper with this evaluation is almost solely due to PB-CPD). With typical commercial papermaking (much less dilute furnish, cycle up of free 3-MCPD), the difference between the competitive G1 resin and the new G1.5 resin would be greater.

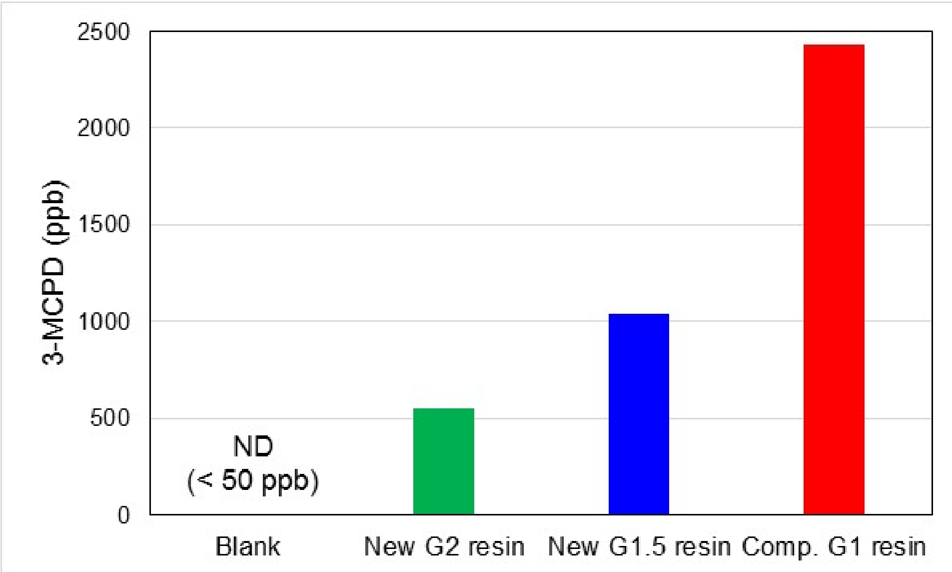

Figure 8 – 3-MCPD in Paper for G2, G1.5 and Competitive G1 Resins due to PB-CPD.

CASE HISTORIES

The following case studies illustrate how improved PAE technology has helped papermakers meet their objectives.

1) **G1.5 PAE Resin Improves Runnability, Performance and VOC**

Using a conventional competitive G1 PAE resin, a southern United States tissue mill observed product efficiency decreases of 12 to 28% during mill storage relative to freshly delivered material. This mill was additionally challenged by having a very high level of fines due to poor fiber quality and low retention. Switching from the conventional G1 PAE resin to the new G1.5 PAE resin resulted in a 14% decrease in resin dosage on a dry basis providing a $256,000 per year savings and an estimated 30 tons reduction of VOC.

2) **G1.5 PAE Resin Improves Runnability, Performance and VOC**

Using a conventional, competitive G1 PAE resin, a northern United States mill manufactures a specialty, wet crepe grade with 95% SWK and 5% broke. Improved performance was needed to achieve the corporate sustainability goal for reduced air pollution emissions. Switching from the conventional G1 PAE resin to the new G1.5 PAE resin resulted in a 60% improvement in the efficiency factor (wet tensile per dosage), a 17% increase in dry tensile and a 47% increase in wet tensile, which yielded a 7% increase in wet/dry performance. Additionally, the turbidity in the dissolved air flotation (DAF) clarifier improved dramatically (turbidity decreased from greater than 40 NTU to less than 2 NTU). The excellent machine runnability lead to a several months long extended trial.

3) G2.5 PAE Resin Contributes to Lower OX in High Wet Strength Towels for Mills using TCF Furnish

Using a G2 PAE resin, a European tissue producer was meeting BfR XXXVI requirements for kitchen towels. However, for high wet strength grades, a key additional parameter to satisfy the specific supermarket customer's requirement was to achieve the TCF target of less than 30 milligram/kilogram of OX in the finished paper product. Using the G2 PAE resin, the mill was unable to achieve this TCF target.

The towel manufacturer conducted trials using a proprietary G2.5 PAE product. The trial results indicated that the efficiency of the G2.5 resin was improved compared to the incumbent G2 resin, achieving the 25% wet/dry tensile target with a 19 grams per square meter (GSM) basis weight product. Analyses at an independent laboratory (ISEGA) of towel samples from the trial indicated much lower OX, 1,3-DCP and 3-MCPD than those obtained with the previous G2 resin program. These results were comfortably within the OX limits set by the Blue Angel ecolabel. These results were achieved for the same cost as the previous G2 PAE resin. Additionally, the proprietary G2.5 resin product contained higher solids, thereby reducing order and delivery frequencies and truck fuel emissions to the environment.

4) New Lower AOX G3 PAE Resin Product Allows Customer to Achieve Strict Local AOX Requirements
A German paper producer that has an effluent discharge close to a municipal water intake is required to meet very strict regulatory limits on AOX in the mill's effluent (500 µg/l). While the mill typically achieved the AOX limits using the incumbent G3 product, the customer wanted to further reduce AOX so that the AOX in effluent level would be comfortably below the limit even when disturbances to the papermaking system occurred. Additional research focused on reducing PBOX content, resulting in a new, proprietary G3 PAE resin that had a higher solids content, a higher AZE content and a 60% reduction in PBOX and AOX content relative to the incumbent product. Customer trials confirmed a 7% increase in the average wet/dry strength and a 60% reduction of AOX in effluent.

SUMMARY

Regulatory drivers and sustainability efforts have resulted in step-change improvements in PAE resin technology that have dramatically lowered 1,3-DCP and 3-MCPD levels to reduce the potential hazard to worker and consumer health and lowered PBOX species to reduce the impact on the environment (AOX of mill effluent) and to allow for the manufacture of TCF grades of paper. Additionally, in gaining an understanding of mechanisms that produce undesired organochloride species, formulations and processes to reduce them were developed, which resulted in improvements in the wet strengthening performance of PAE resins. High solids, high efficiency PAE resins contribute to a smaller environmental impact by allowing the use of less chemistry, less emissions from transportation and less PAE resin (and AOX) in effluent. These attributes fit well with the corporate environmental sustainability programs of major papermakers.

Definitions of Generations and AOX Based on Customer Needs

As PAE resins evolved, the product definitions regarding AOX measurement and the epi by-product definition became inconsistent regarding product "generations" [7]. Table III and Figures 9 and 10 summarize the recommended definition for each product generation (G1, G1.5, G2, G2.5 and G3). These definitions are not arbitrary but are based on key customer needs.

When selecting which generation of technology to use, consideration of external regulatory directives together with the papermakers' own needs is required to meet the guidelines of non-governmental organizations and their own corporate sustainability programs.

Table III – **Recommended Generation Definitions Based on Customer Needs**

Attribute	Generation 1	Generation 1.5	Generation 2	Generation 2.5	Generation 3
1,3-DCP Level (wet product basis)	~10,000 ppm	5,000 ppm	**< 1,000 ppm**	< 700 ppm	< 10 ppm
3-MCPD Level (wet product basis)	> 1,000 ppm	**< 1,000 ppm**	<< 1,000 ppm	< 700 ppm	< 10 ppm
PB-CPD Present in the Resin	Yes	Yes	Yes	**No**	**No**
% **AOX** Level (20% basis)	> 0.80 wt %	< 0.80 wt %	< 0.60 wt %	< 0.25 wt %	< 0.20 wt %
Customer Need	Lowest cost	Not labeled as reproductive toxicant, VOC	No carcinogen warning label	AOX, OX in paper, BfR	BfR, AOX, OX in paper

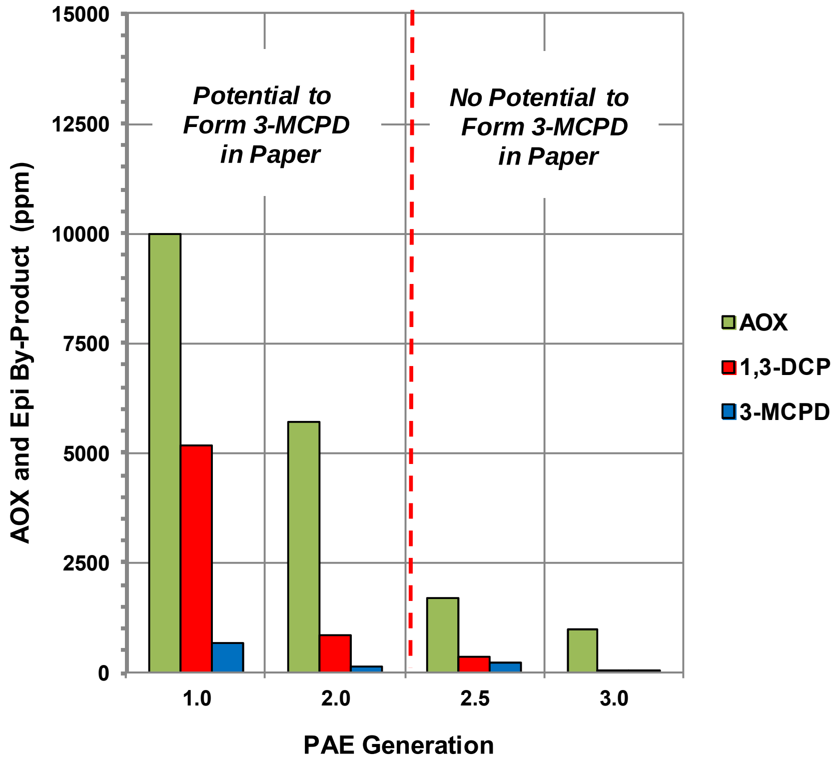

Figure 9 – AOX and Epi By-Product Content for Current PAE Resins.

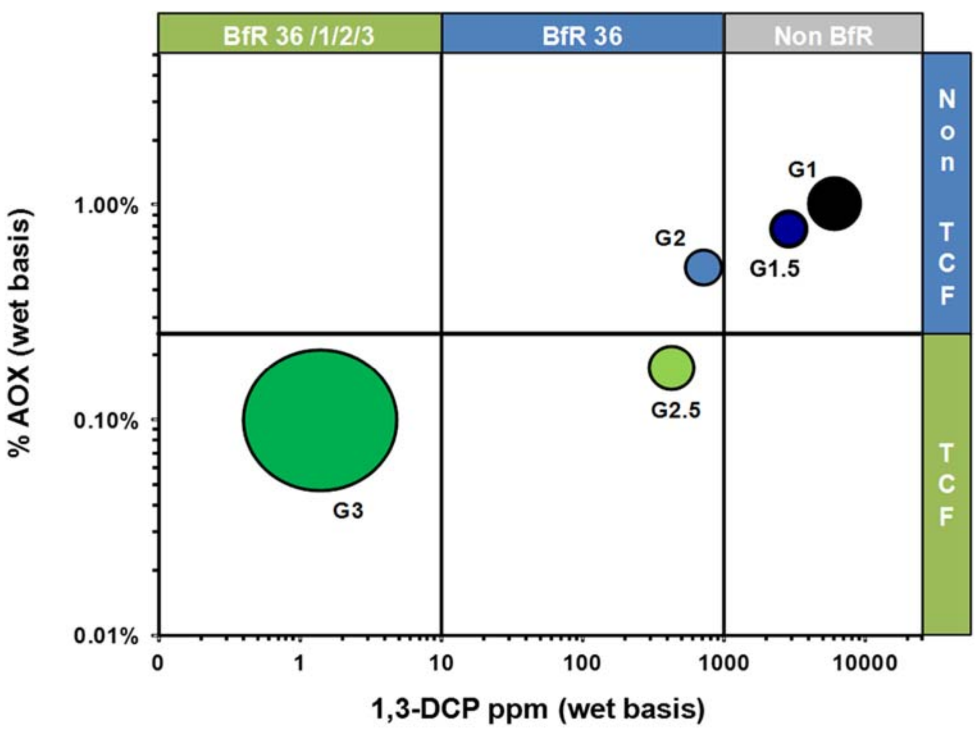

Figure 10 – Paper Compliance Matrix for PAE Resins with Recommended Generation Definitions Based on Customer Needs.

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TISSUE 2017 TAPPI CONFERENCE & EXPO RISI

Regulatory and Sustainability Initiatives Lead to Improved Polyaminopolyamide-epichlorohydrin (PAE) Wet Strength Resins and Paper Products

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Solenis

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Types of Sustainability Directives and Initiatives for PAE Resins

Governmental Regulations	NGO Guidelines	Cost and Performance
Worker safety [e.g., Globally Harmonized System (GHS) SDS's, OSHA, California Proposition 65, Volatile Organic Compounds (VOCs)] using PAE resins	Non-Governmental Organizations' guidelines for product and environment (e.g., EU Ecolabel, Blue Angel, Nordic Ecolabel, Green Seal, paper manufacturers and major retailers)	Maximize solids to minimize transportation (reduce freight cost, carbon dioxide and pollutants), "fewer trucks on the road"
Consumer safety (e.g., FDA, BfR, GB 9685, ANVISA) using paper products made with PAE resins		Resin efficiency at time of customer usage. More efficient resin allows lower dosage, higher retention of PAE (less PAE resin in effluent)
Environmental safety (e.g., GHS, EPA, REACH) using PAE resins (AOX in effluent, aquatic toxicity, VOC)		

Future Perspective on Sustainability Directives and Initiatives for PAE Resins

- Governmental Regulations (examples)
  - New FDA regulations - unlikely
    - New molecules – FCN process
  - State and local initiatives
    - CA Proposition 65, VOC and AOX limitations
  - Impact of GHS on SDS (non-Europe example)
    - Category 1B reproductive toxicity statement
    - “May damage fertility or the unborn child”
  - Move towards BfR type regulations
    - Brazil – ANVISA - June 29, 2018

Future Perspective on Sustainability Directives and Initiatives for PAE Resins

- Non-Regulatory
  - Eco-labels – pragmatic, change partly driven by their customers (paper manufacturers)
  - Major retailers
    - Aldi and Lidl – TCF paper – G2.5 and G3 resins
    - Target Sustainable Product Standard
      - https://corporate.target.com/_media/TargetCorp/csr/pdf/Target-Sustainable-Product-Standard-1.pdf
      - Ingredients - A product contains no ingredients with high level health concerns*. Ingredients with high level of health concern are recognized as carcinogenic, developmental or reproductive toxicants, endocrine disruptors, or have other serious adverse health effects.

* Defined by California EPA Proposition 65 or by European Chemicals Agency as a Substance of Very High Concern

Guidelines from Major Retailers

Target Sustainable Product Standard

Building on Target's commitment to expand its selection of sustainable product choices that effectively balance price, performance and convenience, Target developed a tool to assess products on ingredients, transparency and environmental impact. The Target Sustainable Product Standard will initiate with the personal care, beauty, household cleaning, and baby care product categories.

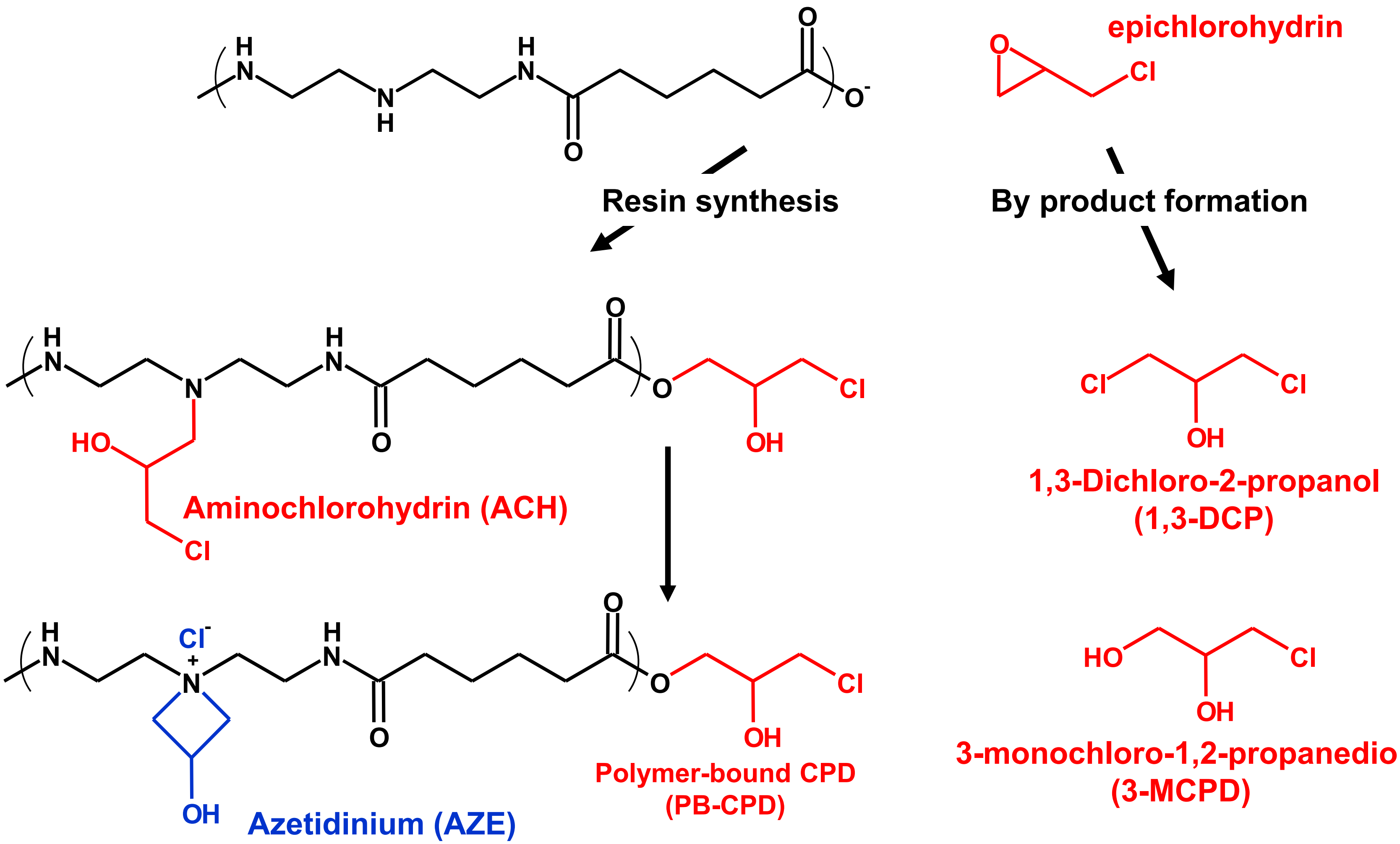
Using the UL Transparency Platform, powered by GoodGuide, Target will collect information from vendors and evaluate products against the standard. Products will receive a score from 0 to 100 (100 being the top score). The more sustainable products will be identified by our standard and rewarded with program incentives. Following the full-assortment assessment, Target will recommend best practices. We plan to use this first phase to learn with our vendors how to improve our entire selection of products. We are also aiming to add other product categories in the near future, including cosmetics in 2014.

Ingredients & Transparency:
A product has been developed with human-health in mind

Issue	Points	Scoring Procedure
Ingredients - A product contains no ingredients with high level health concerns*. Ingredients with high level of health concern are recognized as carcinogenic, developmental or reproductive toxicants, endocrine disruptors, or have other serious adverse health effects.	50	A product will receive zero points if they have one or more ingredients on one of the designated hazard lists. A product with no ingredients on the hazard lists, but do have potentially high hazard in generic ingredients (e.g., unspecified "fragrance" or "surfactant") receive a maximum of 25 points. A product with no ingredients on the hazard lists, but do have potentially low hazards in generic ingredients (e.g., "enzymes") can receive a maximum of 40 points. A product can receive a maximum of 50 points if they have no ingredients on the hazard lists and no generic ingredients.
Transparency - A product's complete ingredient list must be publicly available and disclosed in a way that allows each chemical's health and environmental impacts to be assessed.	20	A product receives a maximum of 20 points if ingredients are listed on packaging and website, ingredient purposes are listed on website and there are no generic ingredients or fully disclosed generic ingredient.

Source – Target Sustainable Product Standard

Typical PAE Resin Manufacture and Formation of Organochlorine Species



Recommended PAE Resin Generation Definitions Based on Customer Needs

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Attribute	Generation 1	Generation 1.5	Generation 2	Generation 2.5	Generation 3
1,3-DCP Level (wet product basis)	~10,000 ppm	5,000 ppm	**< 1,000 ppm**	< 700 ppm	< 10 ppm
3-MCPD Level (wet product basis)	> 1,000 ppm	**< 1,000 ppm**	<< 1,000 ppm	< 700 ppm	< 10 ppm
PB-CPD Present in the Resin	Yes	Yes	Yes	**No**	**No**
% **AOX** Level (20% basis)	> 0.80 wt %	< 0.80 wt %	< 0.60 wt %	< 0.25 wt %	< 0.20 wt %
Customer Need	Lowest cost	Not labeled as reproductive toxicant, VOC	No carcinogen warning label	AOX, OX in paper, BfR	BfR, AOX, OX in paper

State of the art G1 and G1.5 resins have < 1000 ppm 3-MCPD
No category 1B reproductive toxicity SDS statement
No “may damage fertility or the unborn child” statement

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G1, G1.5 and G2 PAE Resins: PB-CPD Contribution to 3-MCPD in Paper

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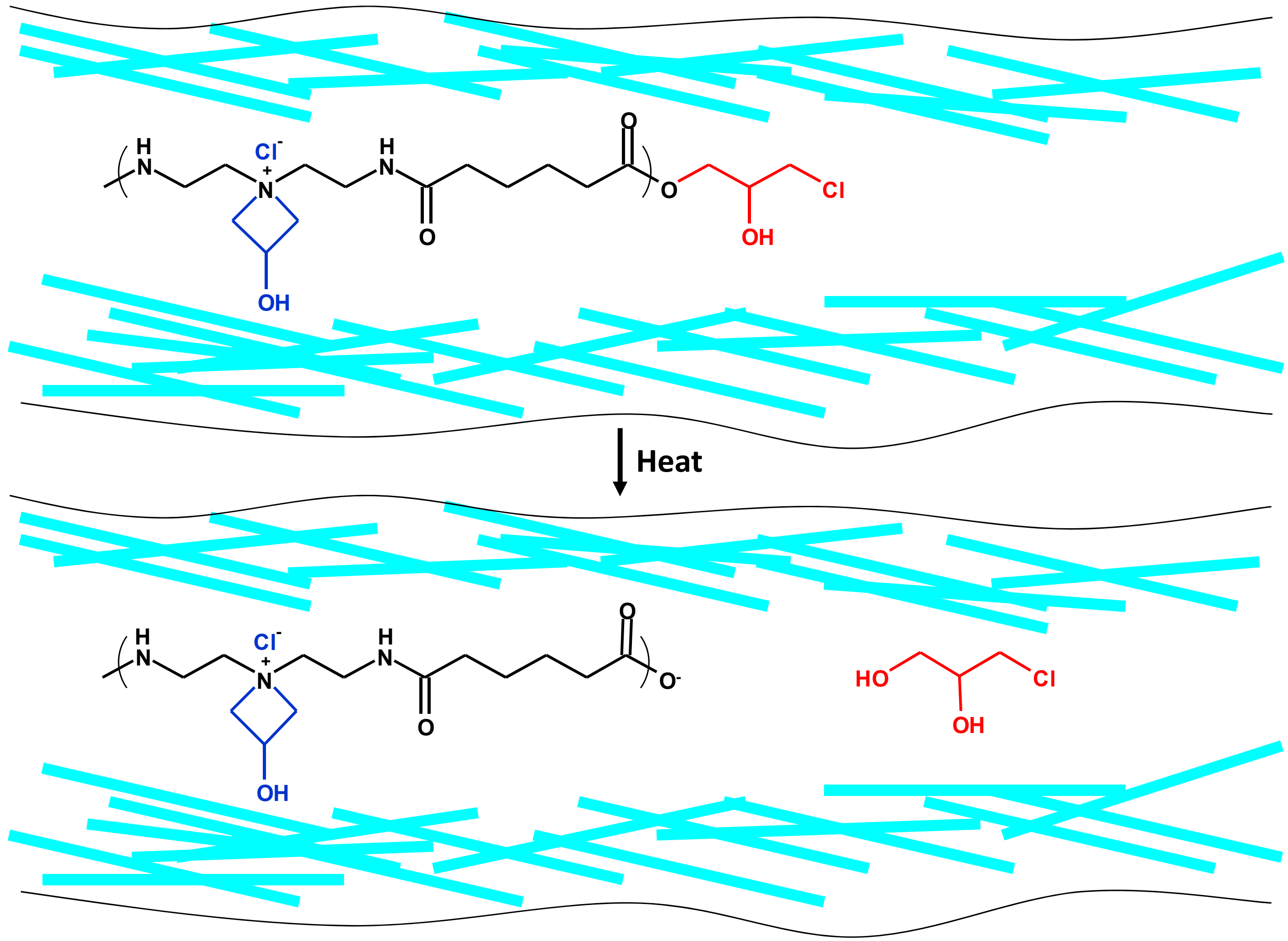
- PAE polymer well retained in the wet web
- Free 1,3-DCP and free 3-MCPD poorly retained, but dependent on water closure
- Main Contribution: Hydrolysis of PB-CPD on PAE polymer in the dryer section



3-MCPD extracted from paper is dependent on both PB-CPD and free 3-MCPD in the PAE resin

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Summary of BfR Recommendations

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Recommended Sample Size and Extraction Method for the Determination of 1,3-DCP and 3-MCPD in Paper Samples							
Sample Type	**Sample Weight**	**Extraction Method**	**Hot/Cold Extraction**	**BfR Limit in Water Extract**		**BfR Limit in Calculated Back to Paper**	
				1,3-DCP	3-MCPD	1,3-DCP	3-MCPD
Teabag/ coffee filter	40g/l (10g/250 mls)	EN647	HOT	2 µg/l	12 µg/l	50 ppb	300 ppb
Kitchen Towel	4g/l (1g/250 mls)	EN645	COLD	2 µg/l	12 µg/l	500 ppb	3000 ppb
Wipes	40g/l (10g/250 mls)	EN645	COLD	2 µg/l	12 µg/l	50 ppb	300 ppb
Other Grades	40g/l (10g/250 mls)	EN645	COLD	2 µg/l	12 µg/l	50 ppb	300 ppb

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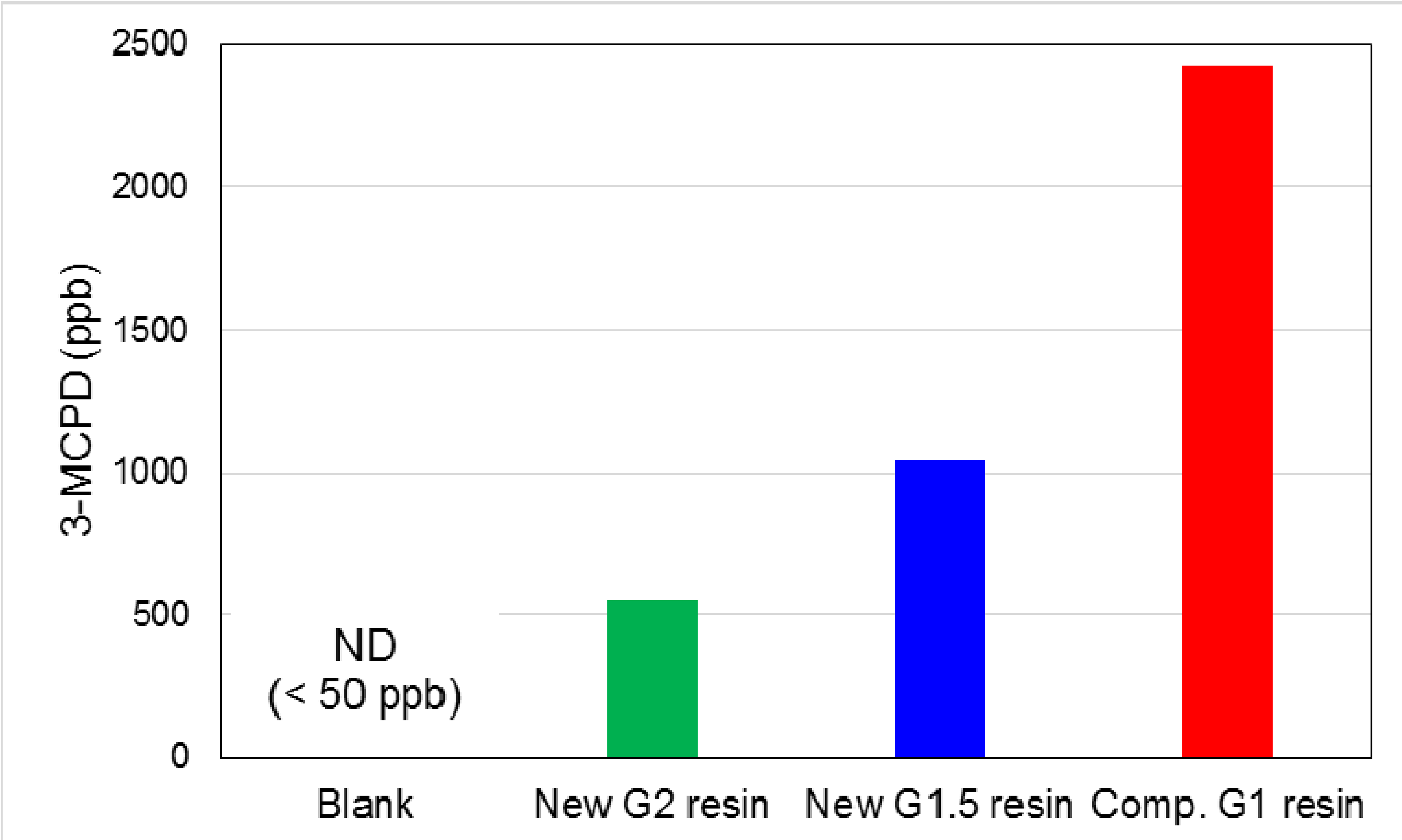
3-MCPD in Paper (due to PB-CPD content) for Different Generation PAE Resins



Handsheet Evaluation

Dosage: 1%, Furnish; 70:30 HW:SW, pH 7.5

Testing: EN645, 1g/250 mls (kitchen towel method)

PAE Resin EH&S Class Summary

Class	Specification	EH&S Attributes
Gen 1	10,000 ppm DCP	SDS carries hazard statements
Gen 1.5	> 25% solids < 5,000 ppm DCP < 500 ppm CPD	No reproductive toxicity hazard Low VOC
Gen 2	< 1,000 ppm DCP Low PB-CPD	No hazard labels Lower VOC
Gen 2.5	< 500 ppm DCP < 500 ppm CPD No PB-CPD	Meet BfR for food contact
Gen 3	< 5 ppm DCP < 10 ppm CPD No PB-CPD	BfR XXXVI 1/2/3 Food contact

Focus on PAE resin Attributes (Gen 1 – Gen 2)

Focus on Finished Paper Attributes (Gen 2.5 – Gen 3)

Optimized NA PAE Resin Products Typical Properties

PAE Resin Type	Total Solids	DCP (ppm)	CPD (ppm)	AOX (ppm)
G1	21%	6,500	750	10,000
New G1.5	**26%**	**5,000**	**475**	**7,500**
G2	20%	<1,000	200	5,500
G2.5	20%	<400	200	1,700
G3	20%	<5	<10	1,000

Case History I: G1.5 PAE Resin Improves Performance and VOC

- Tissue mill located in Southern United States
  - Very high level of fines due to poor fiber quality and low retention
- **Results**
  - 14% decrease in resin dosage (dry basis) relative to competitive G1 PAE resin
  - $256,000 per year savings
  - 30 ton reduction of VOC

Case History II: G1.5 PAE Resin Improves Performance and VOC

- Tissue mill located in Northern United States
  - Specialty, wet crepe grade, 95% SWK and 5% broke
  - Goal: achieve the corporate sustainability goal for reduced air pollution emissions
- **Results** relative to competitive G1 PAE resin
  - 60% improvement in the efficiency factor
  - 17% increase in dry tensile
  - 47% increase in wet tensile
  - **7% increase in wet/dry**
  - DAF turbidity decreased from >40 NTU to <2 NTU
- Improved machine runnability lead to extended trial

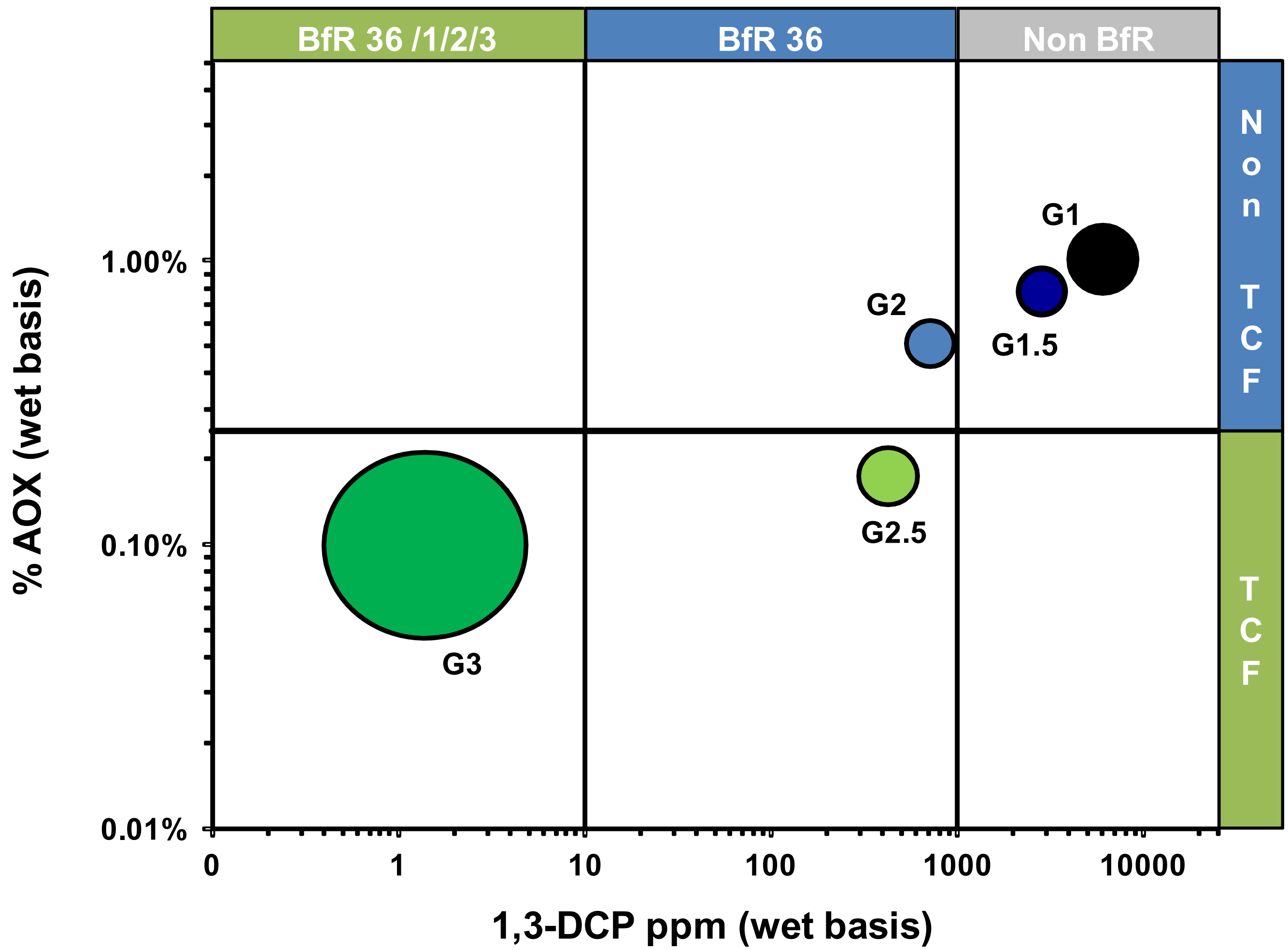
Case History III: G2.5 Resin Provides Lower OX in High Wet Strength Towel Using TCF Furnish

- Specific supermarket customer's requirement
  - TCF target of less than 30 mg/kg of OX in the finished paper product
- **Results**
  - Replaced incumbent G2 resin with proprietary G2.5 resin
  - Improved efficiency, achieving 25% wet/dry tensile target
  - Lower OX, 1,3-DCP and 3-MCPD using independent lab (ISEGA)
    - Comfortably within the OX limits set by Blue Angel
  - No cost-in-use increase compared to the previous G2 PAE resin
  - Higher solids reduced truck emissions to the environment

Case History IV: New Lower AOX G3 PAE Resin to Achieve Strict Local AOX Requirements

- German paper producer required to meet very strict regulatory limits on AOX in the mill's effluent (500 µg/l)
  - Incumbent G3 product too close to limit
- Additional research focused on reducing PBOX content
  - New, proprietary G3 PAE resin
  - Higher solids content
  - Higher AZE content
  - 60% reduction in PBOX content relative to the incumbent G3 product
- **Results**
  - 7% increase in average wet/dry strength
  - 60% reduction of AOX in effluent

Recommended PAE Resin Generation Definitions Based on Customer Needs



Summary

- Results of regulatory and sustainability efforts
  - Much lower 1,3-DCP and 3-MCPD
  - Much lower PBOX species
    - Reduced AOX of mill effluent
    - Ability to produce wet strengthened TCF paper
  - Higher solids, high efficiency PAE resins
    - Reduced transportation emissions, chemistry and PAE resin in effluent
- PAE resin generation selection
  - Dependent on customer need
    - G1.5 instead of competitive G1 – no reproductive toxicity
    - G2 instead of G1 – no 1,3-DCP carcinogen warning label
    - G2.5 and G3 – no PB-CPD for BfR or low AOX