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 for grades requiring wet-strength permanence. 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 past 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 byproducts formed during the manufacturing process of PAE resins. As the levels of these byproducts decreased, the environmental, health, and safety (EH&S) profile of PAE resins and paper products improved. Recent initiatives from major retailers are focusing on product ingredient transparency and quality, thus encouraging the development of safer product formulations while maintaining performance.

PAE resin research over the past 20 years has been directed toward regulatory requirements to improve consumer safety and minimize exposure to potentially carcinogenic materials found in various paper products. One of the best known regulatory requirements is the recommendations of the German Federal Institute for Risk Assessment (BfR), 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 <10 parts per million in the as-received/delivered resin). This paper outlines the PAE resin chemical contributors to adsorbable organic halogens 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).

Application: Paper manufacturers and their customers have key information needed for the proper choice of PAE resin to meet regulatory and sustainability initiatives.

Polyaminopolyamide-epichlorohydrin (PAE) resins are the predominant chemistry used to wet strengthen a diverse range of paper industry products for grades requiring wet strength permanence. First developed and marketed in 1957 [1,2], 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%–35%, under aqueous conditions to fulfill the consumer need.

Following the initial development of PAE resins 60 years ago, resin manufacturers continued to conduct research and 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 [3]. 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 30 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 [4].

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 have varied widely due to market and regional differences. Regulatory directives are the main catalyst for cleaner products with much lower levels of epichlorohydrin byproducts and adsorbable organic halogens (AOX). 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.

BACKGROUND

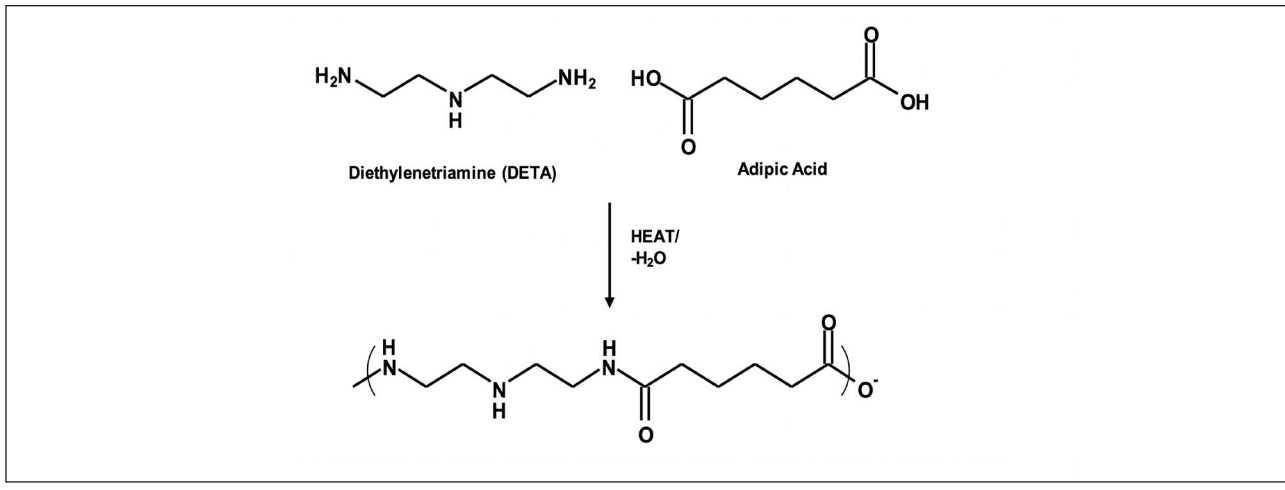
The basic underlying chemistry for the manufacture of a PAE resin has not changed in nearly 60 years [5,6]. A polyaminopolyamide with low molecular weight, known as a prepolymer, is initially formed by polycondensation of adipic acid and diethylenetriamine (DETA), but alternative dibasic acids (and acid derivatives) and polyalkylenepolyamines have been used (Fig. 1). The ratio of the adipic acid and DETA monomers can be varied to provide a prepolymer with higher amine functionality. This prepolymer allows for PAE resins with lower levels of 1,3-dichloropropanol (1,3-DCP) and 3-monochloropropane-1,2-diol (3-MCPD), which are byproducts resulting from side reactions involving the epichlorohydrin (epi) monomer [7,8]. An aqueous mixture of the prepolymer is alkylated with epichlorohydrin at typically 20°C–40°C to initially form tertiary aminochlorohydrin (ACH) functionality. Good temperature control is required to minimize epichlorohydrin hydrolysis and to minimize chloride ion formation [9,10]. After the initial alkylation step, the reaction mixture is typically heated to 60°C–80°C. This step results in further conversion of ACH functionality to azetidinium (AZE) functionality (Fig. 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 typically < 25°C before pumping to storage.

DISCUSSION

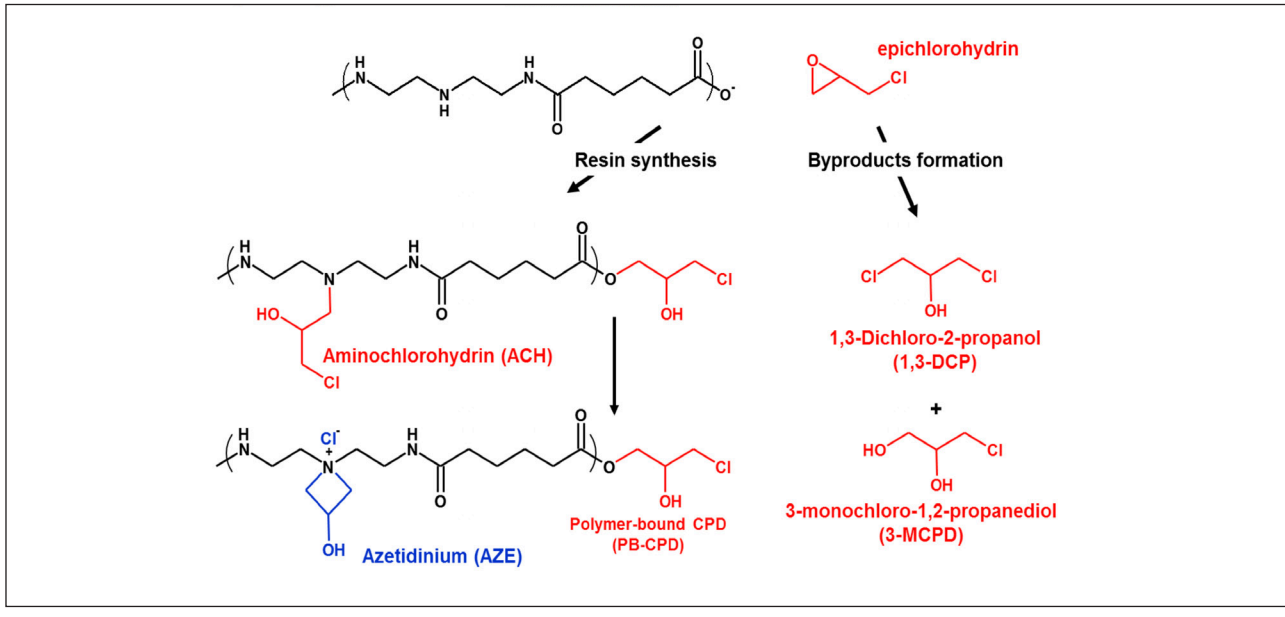
To confirm compliance with governmental directives and nongovernmental organizations' guidelines, the chemistry that affects each directive and guideline must be considered. In PAE wet-strength resins, two types of organic chlorine species exist (Fig. 2): (1) free epichlorohydrin byproducts (1,3-DCP and 3-MCPD) and epichlorohydrin (typically at very low levels) and (2) polymer-bound organic chlorine (PBOX) species. These PBOX species are ACH, the principle species

Governmental Regulations	Nongovernmental Organization Guidelines	Cost and Performance
Worker safety (e.g., Globally Harmonized System [GHS] safety data sheets [SDSs], Occupational Safety and Health Administration [OSHA], California Proposition 65, volatile organic compounds [VOCs]) using polyaminopolyamide-epichlorohydrin (PAE) resins	Guidelines for product and environment (e.g., European Union Ecolabel, Blue Angel, Nordic Ecolabel, and Green Seal, paper manufacturers, and major retailers)	Maximize solids to minimize transportation (e.g., reduce freight cost, carbon dioxide, and pollutants), "fewer trucks on the road"
Consumer safety (e.g., U.S. Food and Drug Administration [FDA], German Federal Institute for Risk Assessment [BfR], Brazil National Health Surveillance Agency [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; U.S. Environmental Protection Agency [EPA]; Registration, Evaluation, Authorization and Restriction of Chemicals [REACH]) using PAE resins (adsorbable organic halogens [AOX] in effluent, aquatic toxicity, VOC)		

I. Types of sustainability directives and initiatives.



1. Typical manufacture of polyaminopolyamide intermediate to polyaminopolyamide-epichlorohydrin (PAE) resin.



2. Typical PAE resin manufacture and formation of epichlorohydrin byproducts.

formed from the initial reaction between epichlorohydrin and the amine groups of the poly(adipic acid-co-diethylenetriamine) prepolymer and PB-CPD, the species formed from the reaction between epichlorohydrin and the acid end groups of the prepolymer. An additional free epichlorohydrin byproduct is 2,3-dichloropropanol (2,3-DCP), which, except for its AOX content, is not regulated. This byproduct is typically at very low levels but can be significant when low-quality epichlorohydrin is used in the PAE resin manufacturing process.

The free epichlorohydrin byproducts and the PBOX species in the PAE resin are interrelated 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 nongovernmental organizations' guidelines, (2) worker safety with PAE resins and epichlorohydrin byproducts, (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 epichlorohydrin byproducts became inconsistent across product generations [11]. These definitions are not arbitrary but are based on key customer needs.

Global governmental regulatory directives and guidelines by nongovernmental organizations

All PAE resins sold as wet-strength resins in the United States, including recently commercialized resins, comply with the U.S. Food and Drug Administration (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 [12]. For the foreseeable future, no new FDA (i.e., no new legal regulatory) requirements are expected in the United States.

However, in the decades since FDA approval of PAE resins, several global governmental directives and nongovernmental 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 German Federal Institute for Risk Assessment (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 National Health Surveillance Agency (ANVISA) has implemented new regulations that took effect on June 29, 2018, and are similar to the BfR recommendations [13]. Before implementation, PAE resin manufacturers and paper manufacturers in Brazil prepared for these changes.

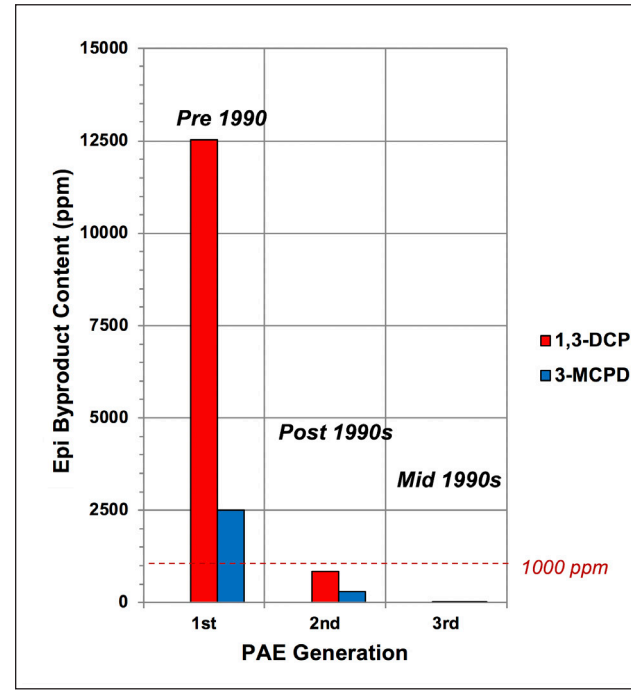
In addition to governmental regulatory directives, guidelines by nongovernmental organizations (i.e., not legally binding) are globally active and can affect PAE resins. The well-known Nordic Ecolabel and EU Ecolabel guidelines restrict the levels of 1,3-DCP and 3-MCPD in PAE resins. Even in the United States, major retailers have announced recent initiatives that could affect the levels of 1,3-DCP and 3-MCPD in food contact packaging [14,15]. Recently, PAE resin manufacturers and paper manufacturers have addressed the impact of California 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, before 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 >0.1% (1000 parts per million [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, epichlorohydrin byproducts, and their impact on worker safety

While epichlorohydrin is used to generate the key reactive functionality (AZE) and structure (molecular weight) for PAE resins, side reactions with epichlorohydrin result in the formation of 1,3-DCP and 3-MCPD. The formation of 3-MCPD is the result of hydrolysis of epichlorohydrin. The formation of 1,3-DCP results from the reaction between epichlorohydrin and chloride ion. The chloride ion is generated from the cross-linking 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 epichlorohydrin present in the wet-strength resin. All three substances are considered to be carcinogenic [16-23]. When first developed, PAE resins had high levels of 1,3-DCP and 3-MCPD (Fig. 3). Freshly produced resins have detectable quantities of residual epichlorohydrin. The level of residual epichlorohydrin rapidly decreases to nondetectable levels (<1 ppm) with all modern PAE resins.



3. The reduction of epichlorohydrin byproducts (12.5% active basis) and the historical definitions of generations 1, 2, and 3 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 1000 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 Europe and the United States). R&D efforts by the major chemical suppliers to reduce the levels of the epichlorohydrin byproducts resulted in what are now known as generation 2 (G2) 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 epichlorohydrin). The resulting resins contained <1000 ppm of 1,3-DCP in the as-received/delivered product [9,10].

With some paper producers looking for resins with levels of epichlorohydrin byproducts significantly lower than 1000 ppm, the R&D efforts of suppliers continued. These efforts resulted in a number of postreaction cleaning techniques that could be applied to G1 or G2 wet-strength resins to reduce the level of epichlorohydrin byproducts to <10 ppm in the as-received/delivered PAE resin products and still provide an acceptable wet-strength response. Post-treatment technologies

include microbial dehalogenation [24-27], membrane filtration [28], and carbon absorption [29–32]. It was discovered that technologies that only removed 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 Fig. 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 [33-40]. These processes essentially 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 [41,42]. An on-site base activation process was developed to remove 1,3-DCP, 3-MCPD, PB-CPD, and AOX [43,44].

For a PAE technology to be classified as generation 2.5 (G2.5) or generation 3 (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 [33-40] 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°C for 24 h. The 3-MCPD level of the 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 <5 ppm, typically <1 ppm. For G1–G2.5 resins, the accuracy of the PB-CPD determination is greatly improved by removing 1,3-DCP and free 3-MCPD to a low level using membrane filtration or other technology on a sample of the PAE resin before the acid test.

To further define the generations of PAE resins, G1 products are those that contain >1000 ppm of 1,3-DCP in the as-received/delivered product. The SDSs for these products must disclose the presence of 1,3-DCP, and they must include a warning regarding the carcinogen hazard of 1,3-DCP. Further, the U.S. 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 SDSs 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 (typically in 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 pictogram
  - Signal word: Danger or warning
  - Hazard statements: H350 or H351 "may cause cancer" or "suspected of causing cancer"; H412 "harmful to aquatic life with long lasting effects"

For G2 wet-strength resins, which contain <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 >1000 ppm of 1,3-DCP typically are not manufactured or imported into the European Union.

The epichlorohydrin byproducts, 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 ecolabels place limitations on the total sum of 1,3-DCP, 3-MCPD and epichlorohydrin 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 epichlorohydrin in the wet-strength resin cannot exceed 7,000 ppm (expressed on a dry basis) [45–47]. 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 epichlorohydrin is at nondetectable levels (<1 ppm) at the time of customer receipt of the PAE resin.

Epichlorohydrin byproducts in paper and consumer safety

Initial concerns about epichlorohydrin byproducts 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 epichlorohydrin byproducts to enter the food chain by migration from various food contact paper grades. After much review and assessment of such risks, the BfR provides a series of recommendations (XXXVI) for the levels of 1,3-DCP and 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 2 µg/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 12 µg/L must not be exceeded in any case" [48].

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).

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 con-

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 Calculated Back to Paper	
				1,3-DCP	3-MCPD	1,3-DCP	3-MCPD
Teabag/coffee filter	40 g/L (10 g/250 mL)	EN647	Hot	2 µg/L	12 µg/L	50 ppb	300 ppb
Kitchen towel	4 g/L (1 g/250 mL)	EN645	Cold	2 µg/L	12 µg/L	500 ppb	3,000 ppb
Wipes	40 g/L (10 g/250 mL)	EN645	Cold	2 µg/L	12 µg/L	50 ppb	300 ppb
Other grades	40 g/L (10 g/250 mL)	EN645	Cold	2 µg/L	12 µg/L	50 ppb	300 ppb

* British Standards EN 647 "Paper and board intended to come into contact with foodstuffs: preparation of a hot water extract" and EN 645 "Paper and board intended to come into contact with foodstuffs: preparation of a cold water extract."

II. Summary of German Federal Institute for Risk Assessment (BfR) XXXVI recommendations.

tact grades, the levels permitted in the paper are one order of magnitude lower.

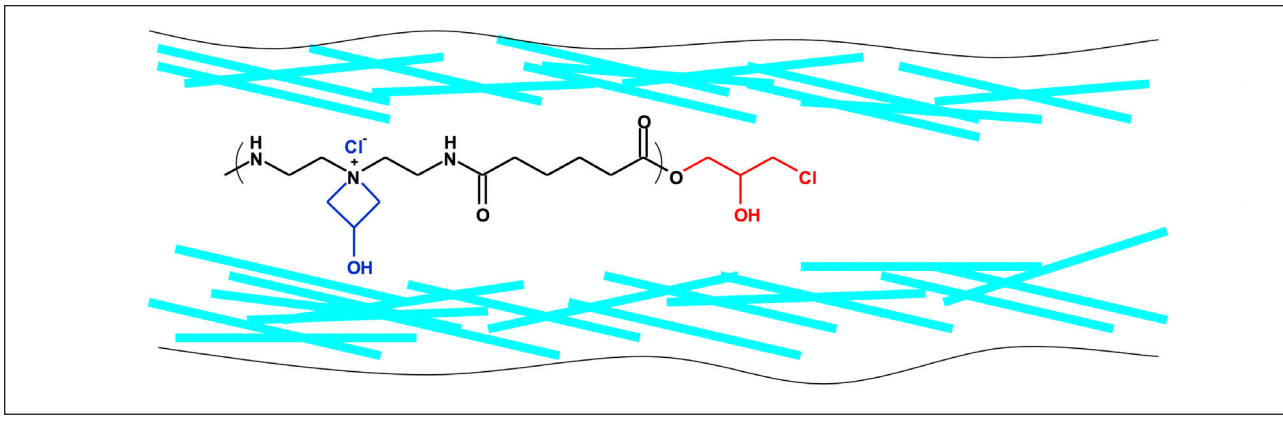
While the recommendations originate from Germany, they have been adopted by the different European countries and European Union institutions (e.g., the 2004 policy statement from the Council of Europe concerning tissue paper, kitchen towels, and napkins) [49]. The recommendations apply to food contact 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 ppm of 3-MCPD in the PAE resin is not likely to result in 1 part per billion [ppb] of 3-MCPD measured in the paper). Paper testing is needed to ensure compliance.

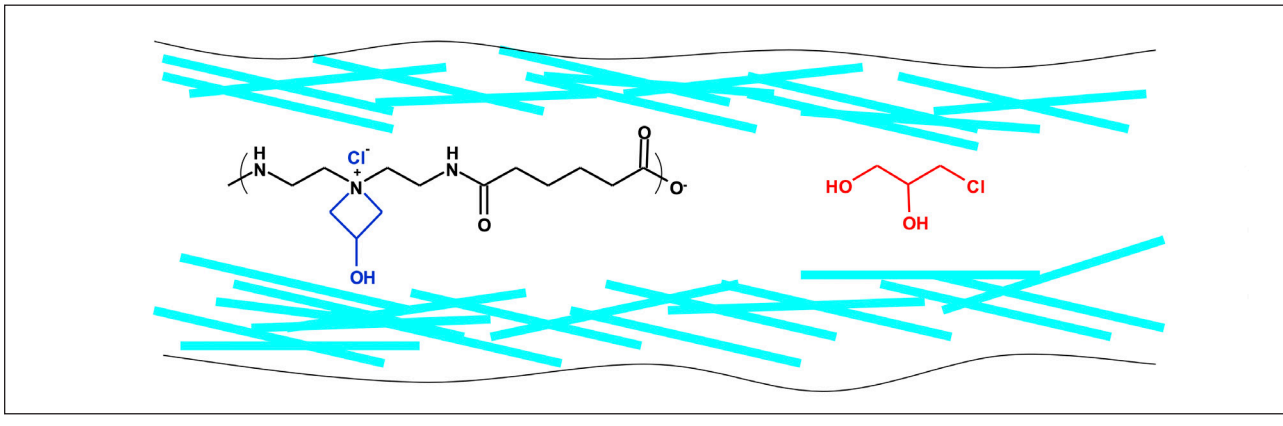
With current PAE resins, an examination of paper test results reveals that the 3-MCPD levels are much higher than the 1,3-DCP levels, even when much more 1,3-DCP is present in the wet-strength resin product. Usually, papermakers struggle to meet the limits for the level of 3-MCPD, whereas the 1,3-DCP 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 epichlorohydrin and acid end groups in the prepolymer (Fig. 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 (Fig. 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 (Fig. 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.

In kitchen towel grades (in paper machines that do not have a high water closure level), resins that contain lower levels of PB-CPD (e.g., G2 resins) typically allow papermakers to manufacture 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 (e.g., napkins, tea bag paper, coffee filters, and liquid packaging board), the paper sample size used in the test method is high-



4. PAE resin polymer retained on fiber and fines in the wet web. 1,3-dichloro-2-propanol (1,3-DCP) and free 3-monochloropropane-1,2-diol (3-MCPD) are poorly retained but will cycle up in the water component of the wet web.



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.

er, 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 nondetectable 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 are 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 increase the overall free 3-MCPD in a resin (e.g., a G2.5 resin), the low substantivity of 3-MCPD to paper fibers (relative to PB-CPD on the cationic polymer) typically results in an overall lower level of 3-MCPD in the paper product. These hydrolysis processes allow post-treatment processes (e.g., microbial dehalogenation or membrane separation) to eliminate the PAE resin contribution to 3-MCPD in paper, resulting in a G3 resin. G3 resins have <10 ppm of 1,3-DCP and free 3-MCPD, but most importantly, they exhibit no potential to generate 3-MCPD due to having very low levels of PB-CPD. Use of G3 resins allows papermakers to manufacture products that meet all the recommendations of the BfR and to meet all of Brazil's ANVISA regulations.

PAE resin effect on AOX and the environment

The epichlorohydrin byproducts, 1,3-DCP and 3-MCPD, are the focus of worker safety and food contact paper regulations. Because of 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. Adsorbable organic halogens is a blanket term that quantifies the amount of organochloride-containing compounds that can be ad-

sorbed onto activated charcoal from water. The term, and methodology used to determine amount, do 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 often is used as a surrogate measure of persistent organic pollutants in the environment.

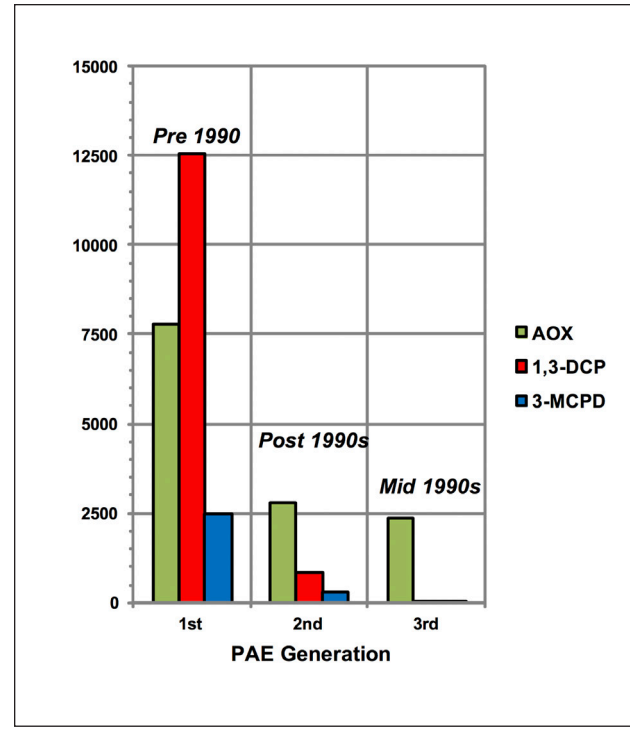
The methods for determining AOX have been standardized worldwide. A number of methods exist, such as U.S. Environmental Protection Agency (EPA) Method 1650C "Adsorbable organic halides by adsorption and coulometric titration," German Institute for Standardisation (DIN) EN 1485 "Water quality—determination of adsorbable organically bound halogens (AOX)," and International Standards Organization (ISO) 9562 "Water quality—determination of adsorbable organically bound halogens (AOX)." 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 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 totally 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 G2 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 G1 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. Resins containing low 1,3-DCP are sometimes referred to as low AOX. However, with G2, G2.5, and G3 resins, PBOX is the primary contributor to AOX in the effluent stream, not the free species 1,3-DCP and 3-MCPD. In the manufacture of a PAE resin, epichlorohydrin reacts with the secondary amine groups of the prepolymer to form ACH. This ACH species then converts to AZE functionality (Fig. 2). Epichlorohydrin 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%–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 because of the greater hydrophilic nature of the 3-MCPD molecule.



6. Adsorbable organic halogens (AOX) content relative to the 1,3-DCP and 3-MCPD content (12.5% active basis), demonstrating the contribution from PBOX species (polymeric aminochlorohydrin [ACH] and PB-CPD).

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. Before 1990, G1 PAE resins had high levels of AOX, mainly because of the high levels of 1,3-DCP present. The development of G2 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 with 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 postreaction cleaning technique to a G2 resin to remove only the 1,3-DCP and the 3-MCPD (Fig. 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.

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 cofactors).

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. As an example, for grades using high PAE resin dosages, the use of an anionic dry-strength agent or an anionic retention polymer is an important factor. 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 epichlorohydrin byproducts 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 TCF. For such grades, the total organic halogen content is <30 mg/kg of dry paper. These grades use TCF pulps, which are produced using oxygen-based bleaching agents (such as ozone, hydrogen peroxide, or both). Methods such as ISO 11480 "Pulp, paper and board—determination of total chlorine and organically bound chlorine" 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 typically is 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 epichlorohydrin byproducts (1,3-DCP and 3-MCPD) for G2, G2.5, and G3 resins. To illustrate this concept, when considering the maximum BfR limits for epichlorohydrin byproducts in paper (kitchen towel), 500 ppb of 1,3-DCP = 0.28 mg/kg of OX in the paper and 3000 ppb of 3-MCPD = 0.98 mg/kg of OX in the paper.

Even at the limits recommended by BfR, free epichlorohydrin byproducts 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.

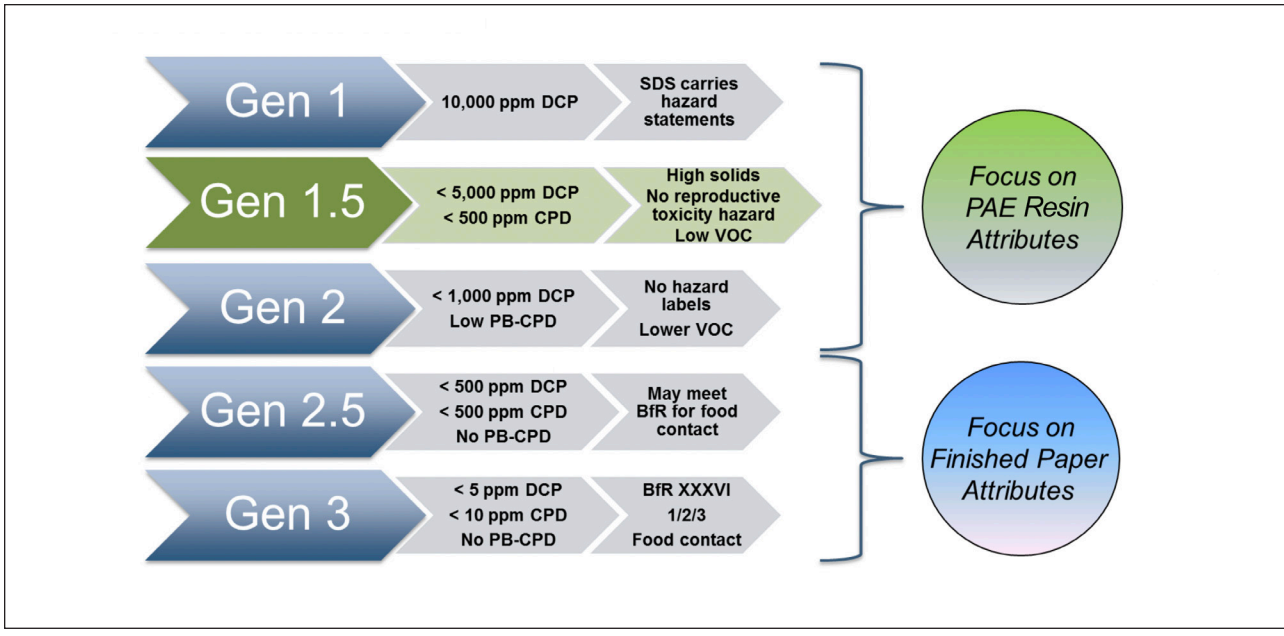
Of the two PBOX species present in the resin, polymeric ACH is the principle source of organic chlorine. The proprietary manufacturing processes for G2.5 and G3 wet-strength resins, which were developed to eliminate PB-CPD species from the final product, also reduce the level of ACH, thereby reducing 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 postreaction 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.

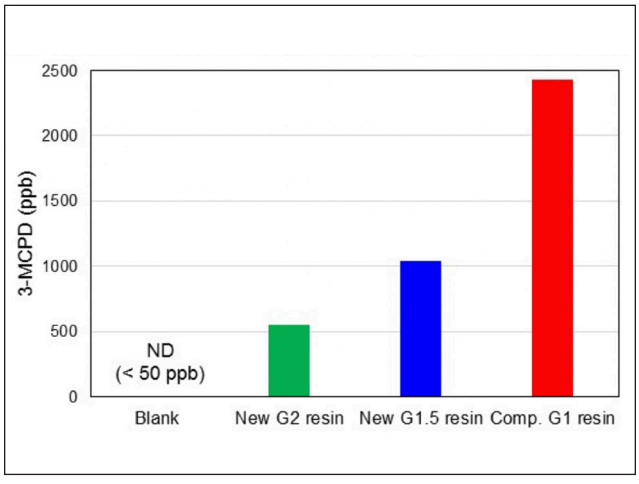
Development of a new class (G1.5) of high-solids, high-efficiency, wet-strength resin products

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 [3] resulted in a breakthrough in G1 resin design such that resins with 12.5%–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. Because 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 <0.1% (1000 ppm) of 3-MCPD, do not indicate category 1B reproductive



7. PAE resin environment, health, and safety class summary.



8. 3-MCPD in paper for generations (G) 2 and 1.5 and competitive G1 resins due to PB-CPD.

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 8 shows 3-MCPD determined in paper, which is dependent on the level of PB-CPD present in 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 hardwood:softwood, and the papermaking was at pH 7.5. The extraction method was British Standards Institute EN645 "Paper and board intended to come into contact with foodstuffs: preparation of a cold water extract" using 1 g of paper for 250 mL of water (i.e., the kitchen towel method). In this evaluation and at equal dry dosage, the new G2 resin has 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 handsheet evaluation using a "Noble and Wood" handsheet device (FORMAX 8 in. x 8 in. stainless steel sheet mold, Adirondack Machine Corp.; Hudson Falls, NY, USA), 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.

CASE HISTORIES

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

G1.5 PAE resin improves runnability, performance, and VOC

Using a conventional competitive G1 PAE resin, a southern U.S. tissue mill observed product efficiency decreases of 12%–28% during mill storage relative to freshly delivered material. This mill was further 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 and provided an average US$256,000/year savings and an estimated 30 tons in reduction of VOC.

Using a conventional, competitive G1 PAE resin, a northern U.S. mill manufactures a specialty wet crepe grade with 95% softwood kraft 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

Attribute	Generation 1	Generation 1.5	Generation 2	Generation 2.5	Generation 3
1,3-DCP level (wet product basis)	~10000 ppm	5000 ppm	<1000 ppm	<700 ppm	<10 ppm
3-MCPD level (wet product basis)	>1000 ppm	<1000 ppm	<1000 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

Abbreviations: 1,3-DCP =1,3-dichloro-2-propanol; 3-MCPD = 3-monochloropropane-1,2-diol; PB-CPD = polymer-bound CPD; AOX = adsorbable organic halogens; VOC = volatile organic compound; OX = organic halogen; BfR = German Federal Institute for Risk Assessment; ppm = parts per million.

III. Recommended generation definitions based on customer needs.

dosage), a 17% increase in dry tensile, and a 47% increase in wet tensile, which yielded a 7% increase in wet/dry performance. The turbidity in the dissolved air flotation clarifier improved dramatically (turbidity decreased from >40 NTU to <2 NTU). The excellent machine runnability led to a several months' long extended trial.

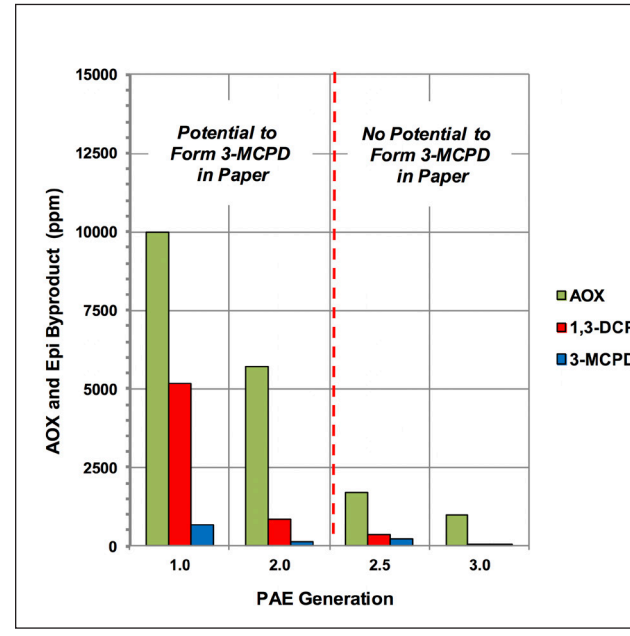
G2.5 PAE resin contributes to lower OX in high wet-strength towels for mills using TCF furnish

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 <30 mg/kg 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 with incumbent G2 resin, achieving the 25% wet/dry tensile target with a 19 g/m^2 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. The proprietary G2.5 resin product contained higher solids, thereby reducing order and delivery frequencies and truck fuel emissions into the environment.

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). The mill typically achieved the AOX limits using the incumbent G3 product, but the customer wanted to further reduce AOX

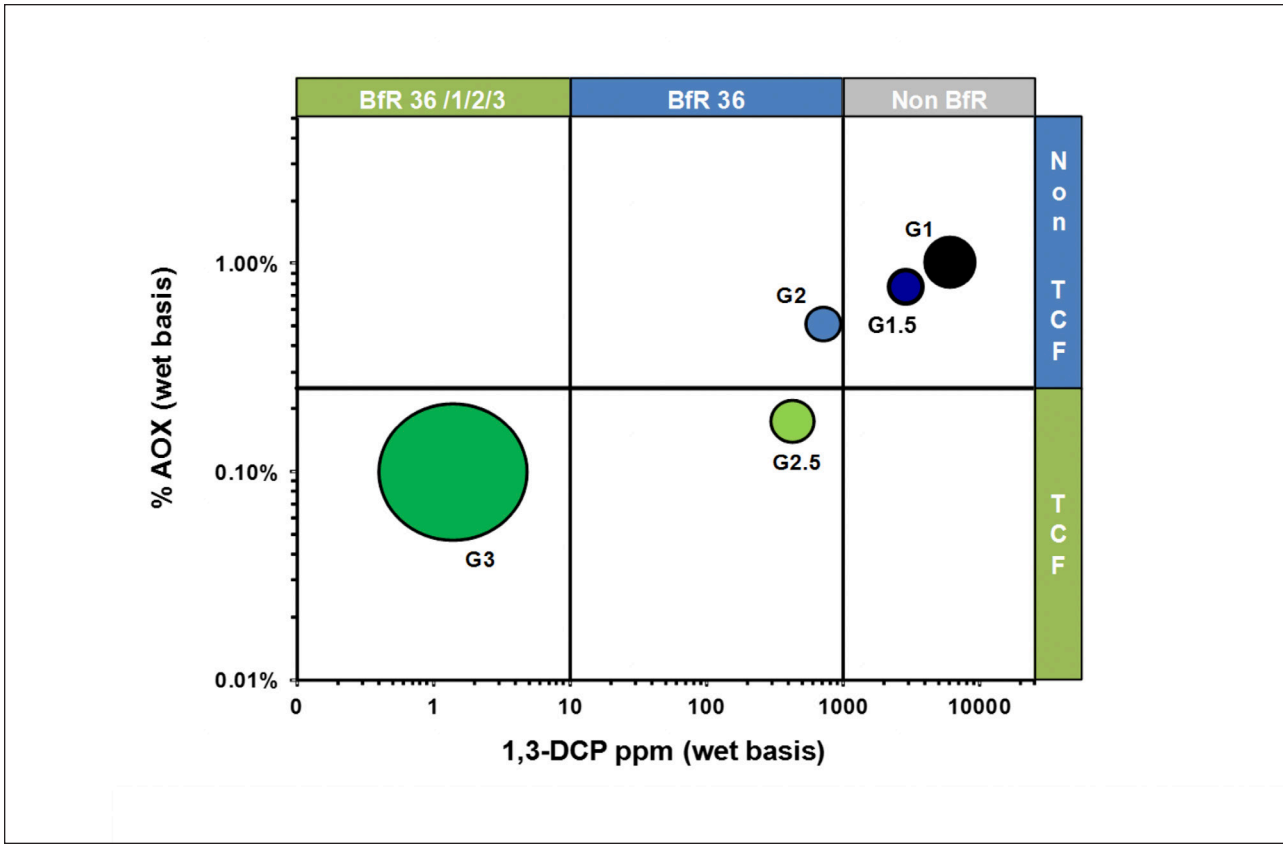


9. AOX and epichlorohydrin byproduct content for current PAE resins.

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. These improvements 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



10. Paper compliance matrix for PAE resins with recommended generation definitions based on customer needs (TCF = totally chlorine free).

for the manufacture of TCF grades of paper. 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 epichlorohydrin byproduct definition became inconsistent regarding product generations [11]. Table III and Figs. 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 papermaker's needs, is required to meet the guidelines of nongovernmental organizations and the papermaker's own corporate sustainability programs. **TJ**

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ABOUT THE AUTHORS

We chose this topic to provide an up-to-date resource to paper manufacturers and their customers regarding the proper choice of PAE resins to meet current regulatory requirements and their customers' specific sustainability initiatives. While this paper is more of a discussion, it is supported by previous patented research and commercial experience, much of which has not been published externally.

The chemistry and applications technology are relatively straightforward to scientific experts, but there are challenges and misunderstandings that act as barriers to proper commercial application. Our hope is that this paper will be a major step forward to address these barriers.

We have discovered the primary causes for 3-MCPD in paper, OX in paper, and AOX in mill effluent and how to address them using a science-based approach. A key finding is that polymer-bound CPD (PB-CPD) is a major cause of 3-MPCD in paper.

For mills, the proper choice of the correct generation of PAE wet-strength resins will allow them to meet their and their customers' needs. This is the guiding theme for this paper and for the definition of each generation.

As regulatory requirements and sustainability initiatives continue to evolve, research will continue into the development of new PAE wet-strength resins to meet these new goals.

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