

Reducing organic chloride contaminants in polyaminoamide-epichlorohydrin wet-strength resins

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ABSTRACT Polyaminoamide-epichlorohydrin (PAE) wet-strength resins contain up to 14% low-molecular-weight organic chloride contaminants. The total organic chloride (TOCl) in these resins consists of unreacted epichlorohydrin as well as dichloropropanol and chloropropanediol, by-products generated during resin synthesis. At commonly used PAE dosages, these TOCl components are distributed throughout the water, paper solids, and atmosphere of papermaking systems in substantial quantities. The work presented here demonstrates that low-TOCl PAE resins can be produced using a modified manufacturing process. Experimental results demonstrate that these low-TOCl resins provide satisfactory wet-strength performance while reducing the level of contaminants by more than two orders of magnitude.

KEYWORDS

Air pollution
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compounds
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Resins
Water pollution
Wet strength
agents

Polyaminoamide-epichlorohydrin (PAE) resins were the first commercially important thermosetting products for use in neutral-to-alkaline furnishes for the manufacture of wet-strength paper. Commercial PAE resins have been approved for use in food-grade papers by the Food and Drug Administration for some time now. The use of these resins increased when it became clear that they could effectively replace the commonly used formaldehyde-containing wet-strength resins. Elimination of formaldehyde was perceived to be desirable for reasons of health and safety, and the PAE resins had the added advantage of superior performance in the form of greater wet tensile strength (1), reduced paper-machine corrosion, and improved paper softness and absorbency.

While the precise mechanism by which PAE resins produce wet strength has not yet been fully defined (2, 3), it is known that the crosslinking reaction between the polyaminoamide and the epichlorohydrin (EPI) is essential (4-6). However, EPI is a

potential pollutant and is subject to strict environmental regulations (7). In addition, the reaction of EPI with hydrochloric acid or water during the standard synthesis of PAE resins (8) has the potential to form by-products such as dichloropropanol (DCP) and chloropropanediol (CPD). Both of these are recognized as potential environmental pollutants (9).

The total quantity of EPI, DCP, and CPD arising from the PAE resin will be referred to in this article as the total organic chloride (TOCl). In papermaking systems, there are many other potential sources for organochlorine contaminants [total organic halides (TOX)], formed primarily during the chlorine bleaching process (10). All of these organochlorine compounds can be sources of environmental contamination because of their solubility in water, their volatility, and their adsorbance on solids in the paper furnish.

In this study, the distribution of TOCl contaminants arising from the use of commercial PAE resins was determined under typical papermak-

ing conditions using both laboratory and paper-mill samples. Procedures for synthesizing PAE resins were modified with the aim of minimizing TOCl content. The wet-strength performance of these low-TOCl PAE resins was then evaluated.

Methods

The preparation of PAE resins is well documented in the patent literature (8). The PAE resins for this investigation were synthesized by adding EPI to an aqueous polyaminoamide base. This base was prepared from the condensation reaction between adipic acid and diethylene triamine. EPI was allowed to react with the base until the desired solution viscosity (degree of crosslinking, or molecular weight) was obtained. The reaction was then stopped, and the system was stabilized by acidifying the resin solution with hydrochloric acid.

EPI, DCP, and CPD concentrations were measured by gas chromatography (Hewlett Packard 5890A) with an electron capture detector.

Samples were extracted with ethyl acetate prior to injection (Alltech AT-WAX columns). The identity of the TOCl components was confirmed by proton NMR (nuclear magnetic resonance) analyses. Commercial PAE products from various manufacturers were used to provide a basis of comparison for the TOCl levels in the resins prepared for this study.

Adsorption isotherms for the PAE resins were obtained on untreated furnish from a paper mill where a commercial PAE resin was in use. Adsorption was also measured on pure cellulose (Sigmacell 100, Sigma Chemicals). The concentrations of PAE resins in the aqueous phase were determined by filtering supernatants through 0.45- μ m nylon filters, followed by titration with polyvinyl-sulfate potassium salt (PVSK), using toluidine blue indicator (11).

Paper handsheets were prepared in the laboratory using a Mark IV dynamic handsheet mold (Paper Chemistry Laboratory) (12). Pressed sheets were conditioned for 16 h at 70°C and 50% RH. Strips of 2.54 cm $\times$ 10.0 cm were cut from the cured sheets and soaked in deionized water for 1 h before measuring their wet tensile strengths on an Instron tester. Dry tensile strength for each sheet was also measured.

Results

TOCl sources

The principal TOCl contaminants in commercial PAE wet-strength resins were identified by both GC and NMR analyses as epichlorohydrin (EPI), dichloropropanol (DCP), and chloropropanediol (CPD). The concentrations of these contaminants in commercial resins from representative manufacturers are listed in Table I.

Resins A and A' are different lots of the same commercial product. Resin A was sampled within one week of production, whereas Resin A' had been in storage for several months. The absence of EPI in Resin A' is therefore indicative of one or more reactions with water, hydrochloric acid, or free amine groups.

Under the standard synthesis conditions used to produce PAE resins, the formation of DCP was found to be a continuous process directly related to the reaction of EPI with the poly-aminoamide backbone. This was dem-

I. Concentration of TOCl components in commercial PAE resins*

Resin	EPI, mg/L	DCP, mg/L	CPD, mg/L	TOCl, %
A	1,045	34,500	4,720	11.50
A'	<200	29,314	3,398	9.66
B	<200	8,764	3,545	13.80
C	<200	7,700	809	2.43

* EPI, DCP, CPD concentrations expressed per liter of product; TOCl is given on a solids basis (g TOCl/g resin solids).

onstrated by removing aliquots from the reaction vessel at selected time intervals and then measuring the EPI and DCP concentrations. Results are illustrated in Fig. 1.

To explain the formation of DCP and CPD during the PAE synthesis process, the reaction mechanism in Fig. 2 was proposed. This mechanism does not include other PAE process steps known to occur, including formation of quaternary groups (13) either by further reactions of EPI with tertiary amines or by cyclization to form azetidinium groups. As explained later in this article, it became clear that to minimize TOCl in a PAE resin product, it would be necessary to optimize process conditions so that the crosslinking (II) and quaternization reactions were favored.

Adsorption experiments

Given the high TOCl concentrations in commercial PAE resins, it is evident that these undesirable components can be distributed throughout the papermaking system. Since PAE resins are generally added just before the paper-machine headbox, an adsorption isotherm for Resin A was obtained by sampling an untreated alkaline furnish of mixed hardwood/softwood (4.0% pulp solids) at the point of addition.

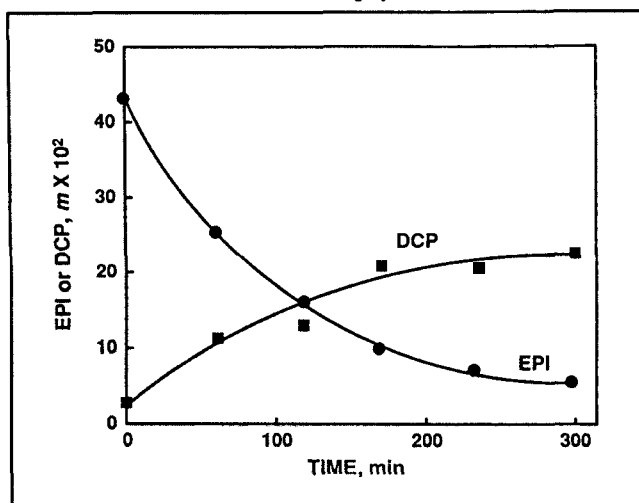
The adsorption of the polymeric resin was expected to be of the high-affinity type exhibited by other highly cationic polymers (14). However, adsorption is also dependent upon the pH of the furnish, as demonstrated by the pH dependence of Resin A's

charge density, q^+ , in Fig. 3. This pH dependence is due to the presence of both tertiary and quaternary amines in the resin backbone.

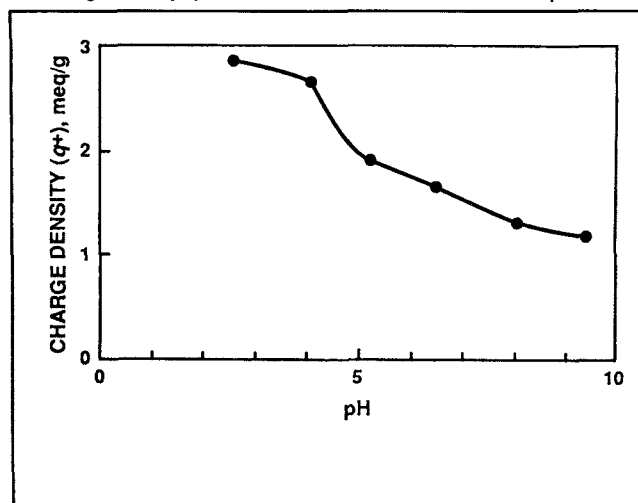
Figure 4 shows adsorption of Resin A on the furnish as a function of resin dosage. Adsorption of Resin A was virtually complete up to very high dosages. The amount of adsorbed resin, plotted as a function of the initial resin dosage, was essentially a straight line with slope close to that for complete adsorption. For example, at a resin dosage of 186 mg/L (0.45% resin solids on pulp solids), which was approximately the dosage used by the paper mill on this furnish, 176 mg/L, or 95%, was adsorbed on the furnish solids. Only at extremely high dosages (above 800 mg/L, far outside those applied in paper systems) did saturation of the pulp occur, leading to classical Langmuir isotherm behavior. Higher-affinity behavior was prevented by the highly swollen fibers in the furnish, which limited mixing, as well as the alkaline pH of the furnish (pH 7.8), which reduced the resin's charge density.

In this adsorption experiment, the TOCl contaminants in Resin A were found to be distributed between the aqueous phase and the furnish solids. The concentration of DCP in the aqueous phase (i.e., unadsorbed DCP) increased linearly with increasing Resin A dosage, as shown in Fig. 5. From the known amount of DCP in Resin A (Table I), the amount of DCP adsorbed on the furnish was estimated to be approximately 30% of the total DCP added. For example, at a resin

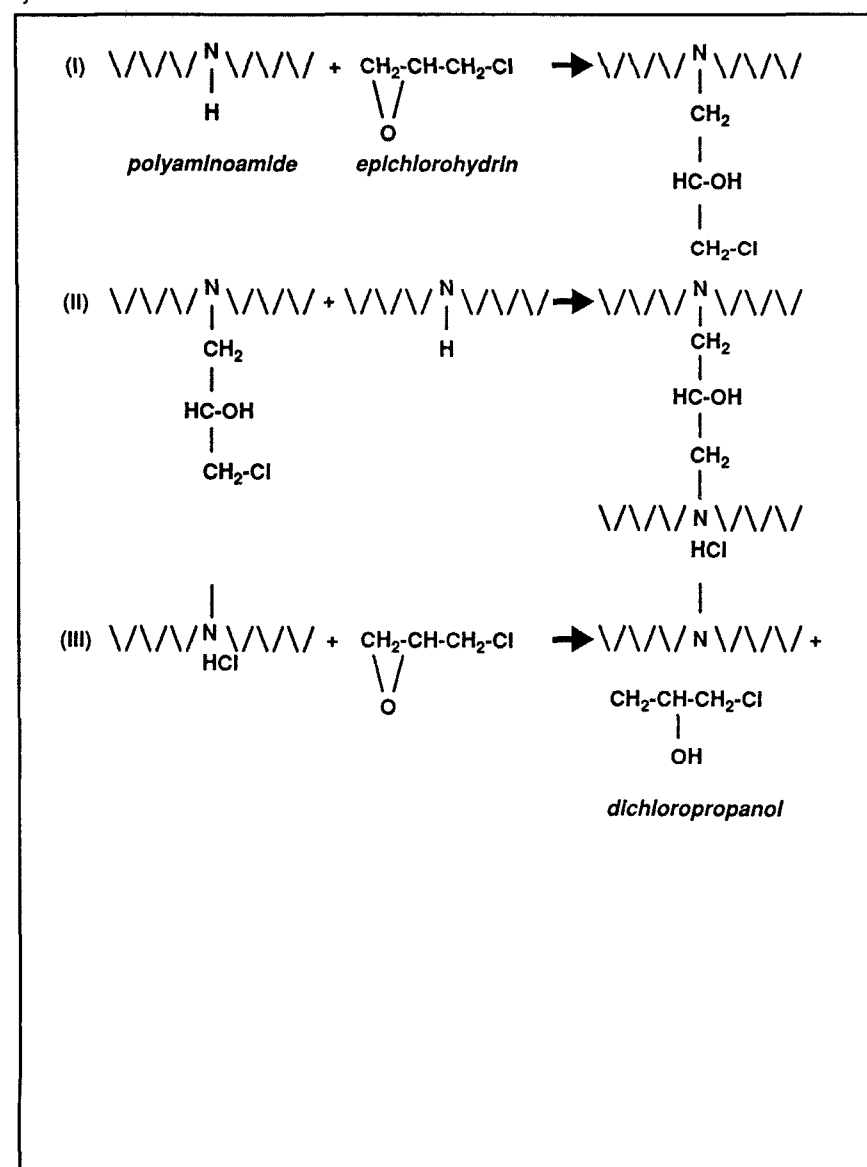
1. EPI and DCP concentrations during synthesis of PAE



3. Charge density, q^+ , of Resin A as a function of solution pH



2. Proposed reaction mechanism for EPI crosslinking (II) and formation of DCP (III) during synthesis of PAE

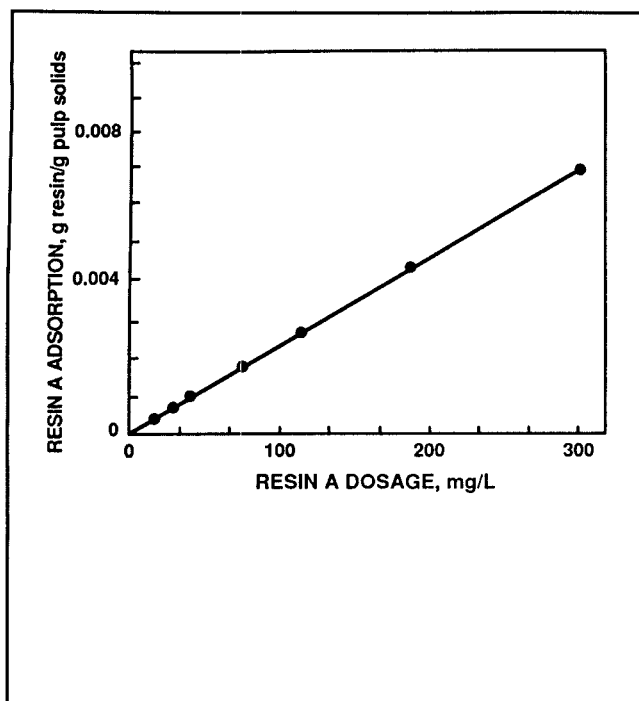


dosage of 186 mg/L, there were approximately 12 mg/L of unadsorbed DCP in the aqueous phase, out of a total of 17.6 mg/L DCP contained in the resin dosage. This estimate neglects the small amount of DCP that would be expected to volatilize, as discussed later in this report. The EPI and CPD concentrations in the aqueous phase were below their detection limits (1 mg/L and 10 mg/L, respectively).

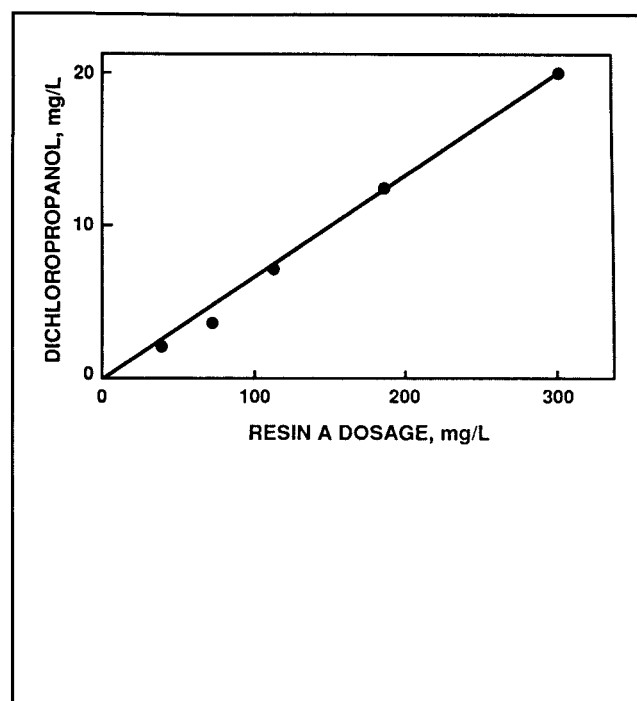
To demonstrate that this behavior is not unique either to Resin A or to the selected mill's furnish, another adsorption experiment was performed with Resins A and C using an aqueous 3% cellulose dispersion adjusted to pH 7.0. This system permitted better mixing, and consequently the adsorption affinities for both resins were found to be of the high-affinity polyelectrolyte type. Results are illustrated in Fig. 6.

As in the case of the paper furnish, the DCP in the cellulose dispersion was distributed between the aqueous phase and the cellulose fibers. (EPI and CPD were again below their detection limits in the aqueous phase.) Again, the concentration of unadsorbed DCP increased linearly with increasing resin dosage, as shown in Fig. 7. However, in this case, 49% of the DCP in Resin C was adsorbed on the cellulose. The adsorption of DCP on cellulose and on paper furnish could be ascribed to hydrogen bonding between the DCP and the hydroxyl and carboxyl functional groups on the cellulosic adsorbents, which is known to result in large adsorption constants (15).

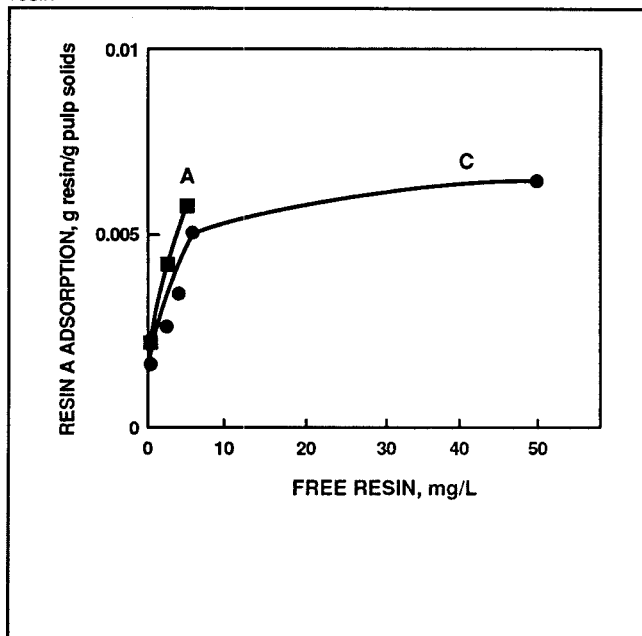
4. Adsorption of Resin A on furnish as a function of resin dosage



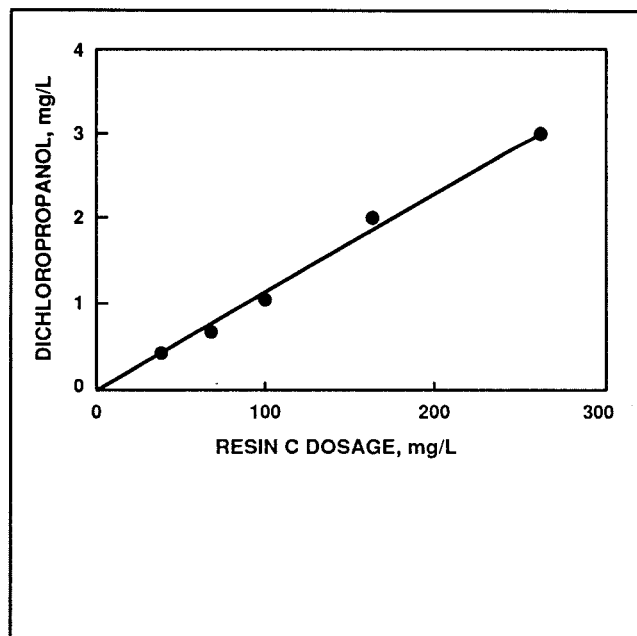
5. Unadsorbed DCP as a function of Resin A dosage



6. Adsorption of Resins A and C on cellulose as a function of free resin



7. Unadsorbed DCP as a function of Resin C dosage



TOCl in white water

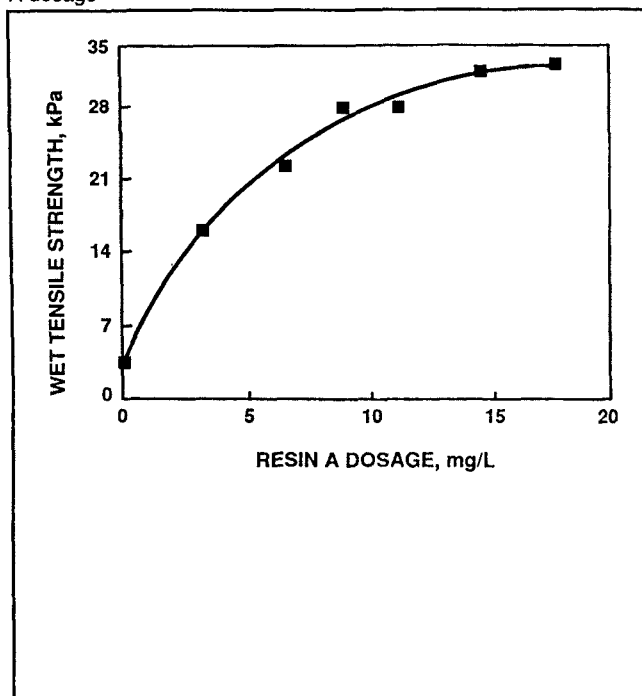
Efforts were made to measure the distribution of TOCl components in the white water from laboratory handsheet preparations. A typical dosage-response curve for the wet tensile strengths of handsheets prepared with Resin A is illustrated in Fig. 8.

Over the resin dosage range tested, the concentrations of EPI, DCP, and CPD in the handsheet white water were all below their detection limits. This dosage range extended well beyond the dosages used in paper-mill furnishes. The difference between the handsheets and the previous adsorption isotherms was that the hand-

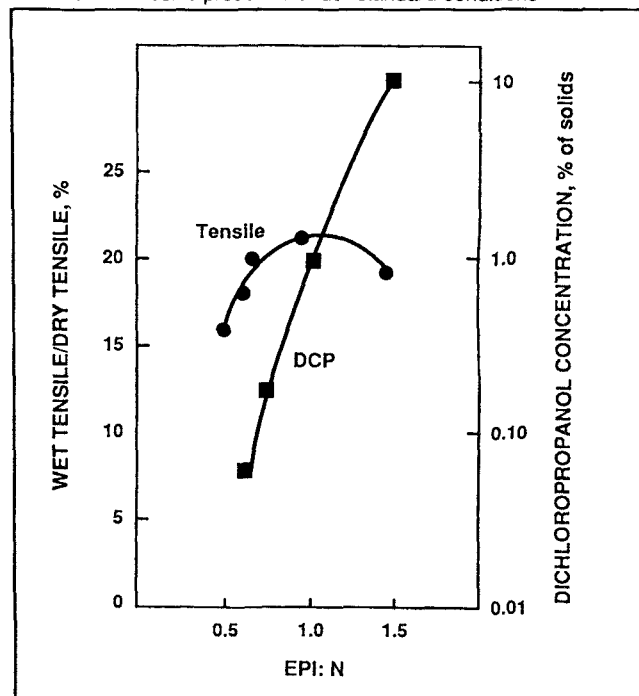
sheets had to be made with paper furnishes of 0.27% paper solids, in contrast to the furnishes used in the adsorption-isotherm experiments, where the solids content was much higher.

Significant concentrations of TOCl were found in all samples taken over a six-week period from a paper mill's

8. Wet tensile strength of laboratory handsheets as a function of Resin A dosage



9. Wet-strength performance and DCP concentration as functions of EPI:N for PAE resins produced under standard conditions



white water. (This was the same mill where the furnish for the adsorption-isotherm experiments was obtained.) The DCP concentrations in white-water samples collected over the six-week span are listed in Table II. The average DCP concentration was 9 mg/L.

During the period when these white-water samples were collected, the stock furnish was receiving a Resin A' dosage of 124 mg/L. However, because of dilution in the head-box, this resin dosage only contributed 2 mg/L DCP to the system. Hence, the higher DCP concentrations found in the system were ascribed to white-water recycle effects, leading to gradual accumulation of TOCl.

Assuming that the DCP in the resin dosage behaves in accord with the adsorption-isotherm data, there would be an expected 30%, or 3 mg/L, of DCP adsorbed on the furnish solids in equilibrium with the 9 mg/L DCP in the aqueous phase. The concentration of TOCl contaminants distributed throughout a papermaking system would be, on the basis of these data, directly proportional to the TOCl content of the wet-strength resin in use.

Atmospheric discharge of TOCl

The discharge of aqueous TOCl and

other TOX components is expected to come under very stringent guidelines worldwide. For example, a limit of 0.1 mg TOX/L has been set in Germany, and efforts have been made to reduce TOCl in PAE resins sold there (16).

The effects of the resin TOCl content on air pollution would at first seem to be negligible. In a closed system, the air in equilibrium with white water containing 9 mg/L DCP would contain less than 0.1 mg/L DCP. This quantity was estimated from Henry's law, assuming a Henry's law constant on the order of 10^{-4} atm $\cdot$ m³/mole (17). Assuming that EPI and CPD behave similarly, the amounts of these materials in the air would be an order of magnitude less than that of DCP. Since the TLV (threshold limit value) for EPI was established as 2 ppm (18), and since operating paper mills are well-ventilated open systems, it was concluded that evaporation of TOCl components from the white water would not pose a serious environmental problem.

This observation could be offset by considering the TOCl components that might volatilize in the paper-machine dryer section. Paper sheets entering a dryer section typically contain about 70% water (19), while the finished, dried sheets contain less than 5% water. Thus for each metric

ton of finished paper produced, 2.2 metric tons of water must be driven off. Then, assuming the water contained 9 mg/L TOCl, there would be 20 g TOCl driven off into the atmosphere for every metric ton of finished paper produced. These calculations neglect any desorption of the TOCl components from the paper fibers during the drying process. The environmental impact of this process is not simple to estimate and may require extensive field studies to fully define. However, it is clearly desirable to find a way to minimize the quantity of TOCl contaminants in PAE wet-strength resins.

Low-TOCl resins

The most obvious way of reducing the TOCl contaminants in PAE resins is to reduce the ratio of EPI to poly-aminoamide used in the standard PAE synthesis process. This molar ratio can be expressed as EPI:N, where N represents the secondary amine equivalents in the poly-aminoamide. The effects of EPI:N on wet-strength performance and TOCl content are illustrated in Fig. 9.

Reducing the EPI:N ratio in the standard PAE-synthesis method decreased both the TOCl and the wet-strength performance. For example, at an EPI:N of 0.5, the DCP concen-

tration in the resin product decreased by more than two orders of magnitude, but the wet strength also decreased by 24%. This unacceptable loss in wet strength was due to (a) the loss of sufficient quaternary charge density in the resin for adsorption and (b) the loss of sufficient crosslink density for tensile strength (20).

To minimize TOCl while maintaining acceptable wet-strength activity, a series of 27 statistically designed PAE-synthesis experiments was performed in an effort to identify the optimum process variables, including temperature, concentration, reaction time, and feed rate. The optimum process variables identified were then used to prepare PAE resins with EPI:N ranging from 0.7 to 1.5. Each of these resins was tested for TOCl content and evaluated for wet-strength activity in handsheets made with three different furnishes. The results of these experiments are summarized in Table III.

From these results, it was concluded that a PAE resin with acceptable wet-strength performance in a wide variety of paper furnishes could be prepared with from 25 times (EPI:N = 1.0) to 200 times (EPI:N = 0.7) less TOCl than the PAE resins now on the market. Resins made with EPI:N < 1 using the optimized production procedures showed TOCl concentration far below the detection limits in the aqueous phase of adsorption isotherms as well as in handsheet white waters.

The maximum amount of TOCl that could be present in a paper mill's headbox feed, when using the EPI:N = 0.7 resin at a dosage of 0.4%, was calculated to be 0.054 mg/L. That is, the low-TOCl resin would reduce the free TOCl in the mill system by more than two orders of magnitude compared with the 9-mg/L levels found in mill white water (Table II). This in turn would result in more than a two-orders-of-magnitude reduction in the TOCl discharged to the atmosphere from the dryer section, from 20 g TOCl/metric ton of paper to less than 121 mg TOCl/metric ton.

From the data in Table III, it was recognized that a small reduction in wet-strength performance could occur in some mill furnishes for the low-TOCl resin with EPI:N = 0.7. This can be compensated by a small increase in dosage, as well as by other minor

II. TOCl concentrations in mill white water

Sample	EPI, mg/L	DCP, mg/L	CPD, mg/L
1	<1	8.0	<10
2	<1	3.2	<10
3	<1	8.6	<10
4	<1	10.2	<10
5	<1	9.6	<10
6	<1	12.8	<10

III. Effects of EPI:N in optimized process on wet strength and TOCl content

EPI:N	Furnish ^a	Tensile ratio ^b	Resin TOCl, % ^c
0.7	1	0.85	0.045
	2	0.92	
	3	0.99	
0.8	1	0.83	...
	2	1.05	
0.9	2	1.34	...
1.0	1	1.03	0.37
	2	1.39	
	3	1.04	
1.1	1	1.17	0.96
1.2	1	1.25	1.2
A'	1	1.00	9.7
	2	1.00	
	3	1.00	

^a 1 = mixed hardwood-softwood kraft; 2 = softwood kraft; 3 = mixed softwood sulfite.

^b Wet tensile ratio defined as the wet tensile strength (psi) relative to the commercial A' resin, both at 11 mg/L (8 lb/ton) dosages

^c TOCl on a solids basis (g TOCl/g resin solids)

chemical and production-system alterations.

Conclusion

Current commercial PAE resins contain as much as 14% TOCl contaminants on a resin solids basis. Under commonly applied dosage conditions, this leads to the presence of approximately 9 mg/L TOCl free in the paper-furnish aqueous phase and white water, with an additional 3 mg/

L TOCl adsorbed on the furnish solids. The discharge of this white water was recognized as a potential problem for paper mills, which must operate under strict environmental regulations for effluent water quality. Also, the volatilization of the water in the dryer section leads to atmospheric discharge of as much as 20 g TOCl per metric ton of paper produced.

By optimizing the parameters of the synthesis process and modifying the EPI:N reactant concentrations, it was

possible to produce resins with low levels of TOCl contaminant while maintaining a high level of wet-strength performance. For example, a PAE resin made with the optimized process and a ratio of EPI:N = 0.7 contained only 0.045% TOCl contaminants. The low-TOCl resin was shown to be capable of reducing the TOCl in the paper furnish from 9 mg/L to 0.054 mg/L. This would reduce the atmospheric discharge of TOCl from the dryer section to less than 121 mg TOCl per metric ton of paper produced. While these improvements are significant, research to further reduce or eliminate TOCl contaminants from wet-strength resin products is ongoing. □

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