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COOLING WATER



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Cooling

Performance Review of Simplified Cooling Water Treatment

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Effective corrosion and deposit control in evaporative cooling circuits can generally be achieved by selection and formulation of a phosphate, phosphonate, polymer dispersant, and azole treatment, with the possible supplement of zinc for highly corrosive systems.

Unfortunately, formulating for effective corrosion and deposit control without increasing treatment costs is not that simple. Faced with the manufacture and supply of safe, high performance, cost-effective programs, the water treatment professional must choose from a wide array of formulation components. Often a water treatment chemical supplier is tempted to develop sophisticated, multi-functional formulations based on numerous components. However, increasing their number only adds to inventory and manufacturing costs.

To assist with simplifying corrosion and deposit control formulation development, the water treater often relies on models. These models consist of: 1. prescriptions for a suite of starting-point formulations (1); 2. a combination of field experience and an understanding of saturation indices, silt, and iron contamination; and 3. computerized models for optimization of inhibitor ratios (2). Each modeling approach requires a good understanding of the performance envelope of individual scale and corrosion inhibitors, together with knowledge of the target cooling system operating range.

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With rising raw material costs, a more competitive water treatment market, and a customer base struggling with economic recovery and growth, water treatment companies have been forced to re-examine the cost and composition of their product formulations (1). Specifically, the need for the complexity of a large number of components, which in turn requires high product inventories, has come into question. Formulators are also challenged with responding to increasing sensitivity toward environmental discharge limits. As a result, they are turning toward the use of more environmentally benign corrosion and scale inhibitors in lieu of phosphates, zinc, and manganese. Instead, they are focused on the pursuit of formulation cost reductions that do not compromise environmental impact and product performance. New chemistries are therefore sought to form the basis of a simplified, flexible range of all-organic cooling circuit formulations that can also sustain high corrosion and deposit control performance.

Evolution of EPOC

The mid-1990s saw the introduction of a novel polymer chemistry: phosphono carboxylic acid (POCA). For the first

time, the performance properties of both phosphonate and polymer were combined into one molecule. The performance of POCA has been profiled (3), and it was recommended as a new building block for a new generation of cooling water treatment programs. This unique polymer chemistry has since been subject to extensive process development and performance optimization, ultimately resulting in the launch of enhanced phosphono carboxylate, or EPOC.

BWA Water Additives^a manufactures EPOC via a proprietary polymerization process, and continues to profile EPOC performance through lab and field studies. Through a combination of pilot cooling water and mild steel corrosion experiments, the supplier's U.K. laboratories have revealed how the scale and corrosion inhibition properties of EPOC match those of hydroxy phosphono acetic acid (HPA), 1-hydroxyethylidene-1,1-diphosphonic acid (HEDPA), and phosphono polymaleic acid (PPMA). Further, by the direct performance comparison of EPOC to formulations comprising sulfonated copolymer (S-Co) and HEDPA, the feasibility of substituting two scale and

TABLE A
Corrosion Test Water Chemistries

	Ion Concentration		
	50 mg/L Ca Water	150 mg/L Ca Water	300 mg/L Ca Water
Calcium as CaCO ₃	50 mg/L	150 mg/L	300 mg/L
Magnesium as CaCO ₃	25 mg/L	75 mg/L	150 mg/L
Total alkalinity as CaCO ₃	15 mg/L	350 mg/L	300 mg/L
Chloride as ion	29 mg/L	200 mg/L	212 mg/L
Sulfate as ion	18 mg/L	200 mg/L	142 mg/L
Initial pH at 40°C	7.0	8.5	8.3

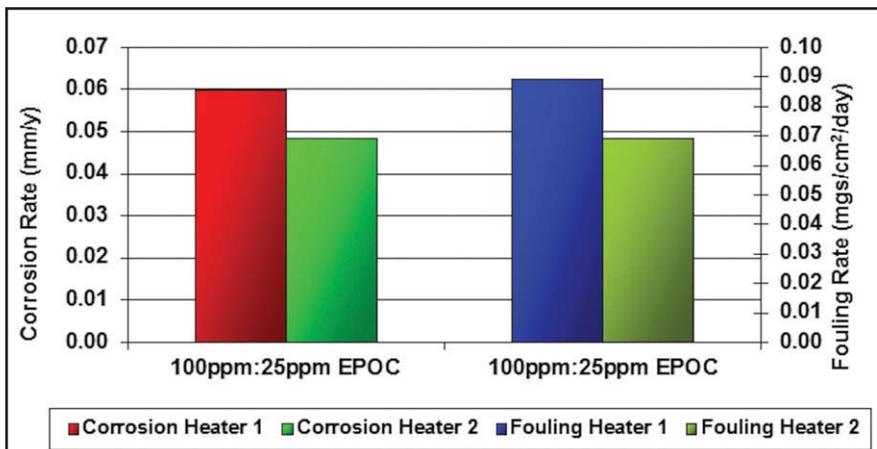


Figure 1. Pilot cooling unit corrosion and fouling rates in 50-Ca water.

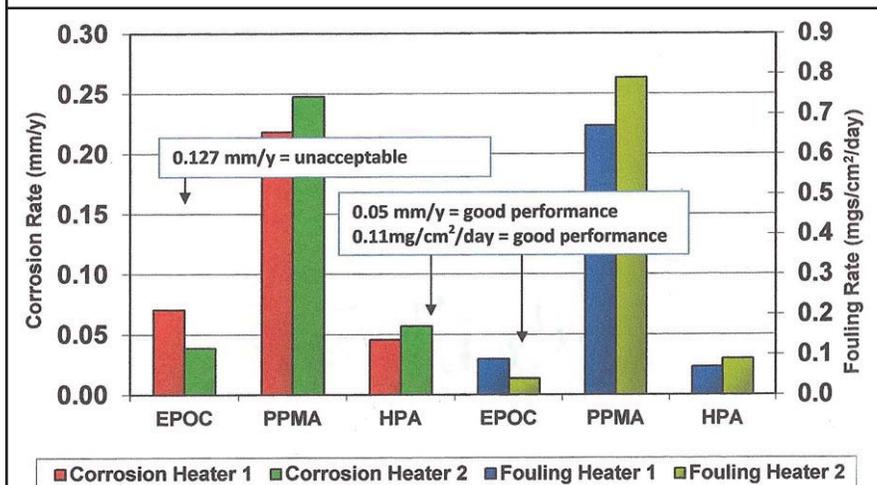


Figure 2. Pilot cooling unit corrosion and fouling rates in 150-Ca water. Dose level: 80 mg/L high level; 20mg/L maintenance.

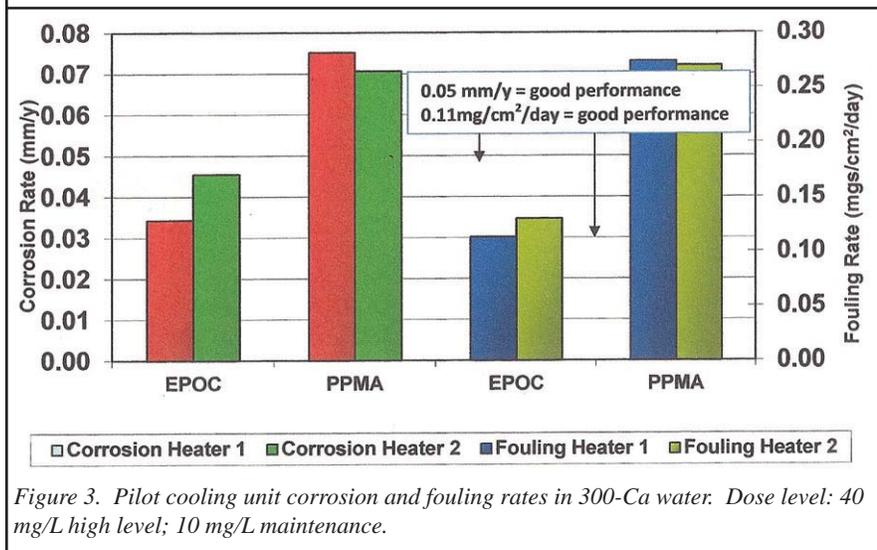


Figure 3. Pilot cooling unit corrosion and fouling rates in 300-Ca water. Dose level: 40 mg/L high level; 10 mg/L maintenance.

corrosion inhibitors used in conventional formulations, by EPOC alone, has been demonstrated.

The multifunctional nature of EPOC

is an answer to the water treater's challenges as set out above. Formulating with EPOC will maintain a forgiving, broad performance profile, within an

all-organic program, while allowing the water treater to simplify formulations and reduce supply chain costs.

Fouling and Corrosion Control

To simulate the conditions encountered in recirculating cooling water systems as closely as possible, the supplier's U.K. laboratories operate pilot cooling units to assess the performance of new scale and corrosion inhibitors. Details of these units have been disclosed previously (4). Water chemistries used in various rig runs are listed in Table A. Water is recirculated continuously over two pre-weighed mild steel heat exchangers, and a coupon chamber containing pre-weighed specimens of different metallurgy. The system is heated via two heat exchangers, each having a heat flux of 10,000 British thermal units per square feet per hour (Btu/ft²/hr) (31,520 watts per square meter [W/m²]), and cooled by means of a cooling coil, operated by a solenoid valve activated by a control system.

Corrosion and fouling data from several rig runs are summarized in Figures 1 through 3. Figure 1 demonstrates how corrosion control is possible in a severely corrosive soft water (50 milligrams per liter [mg/L] calcium [Ca]) with EPOC alone. In this example, the dose level was 100 mg/L solids for the 3-day high level followed by 11 days at the lower 25 mg/L solids dose level. The two heat exchanger corrosion rates were good at 0.0599 millimeters per year (mm/y) (2.36 mil per year [mpy]) and 0.0484 mm/y (1.91 mpy), respectively. The fouling rates were excellent at 0.089 milligrams per square centimeters per day (mg/cm²/d) and 0.069 mg/cm²/d.

Figure 2 compares EPOC with PPMA and HPA in a 150-mg/L Ca water in which high chloride and sulfate ensure aggressiveness, as evidenced by control corrosion rates of 0.403 mm/y (15.87 mpy) and 0.492 mm/y (19.35 mpy). The control fouling rates were 1.519 mg/cm²/d and 1.744 mg/cm²/d, respectively. Dose levels used in this water were 80 mg/L as solids for the high level 3-day period decaying to 20 mg/L solids for the 11-day maintenance period. Good corro-

sion rates were obtained on the two-day heat exchangers for both EPOC (0.071 mm/y, 2.78 mpy) and 0.039 mm/y (1.52 mpy) and HPA 0.046 mm/y (1.79 mpy) and 0.057 mm/y (2.24 mpy). However, the PPMA gave unacceptable corrosion rates on both heat exchangers at this dose level (0.218 mm/y or 8.6 mpy, and 0.248 mm/y or 9.75 mpy).

Unsurprisingly, the fouling rate for the PPMA was also unacceptable at 0.67 mg/cm²/d and 0.79 mg/cm²/d, respectively. In comparison, scaling rates for both the EPOC (0.088 mg/cm²/d and 0.04 mg/cm²/d) and HPA (0.069 mg/cm²/d and 0.09 mg/cm²/d) were very good.

Figure 3 compares EPOC in a higher Ca water of 300 mg/L Ca. As expected in this higher Ca water, the corrosion rates decrease over those in both the 50-mg/L and 150-mg/L Ca waters as demonstrated by the control corrosion rate result of 0.223 mm/y (8.78 mpy) and 0.252 mm/y (9.92 mpy). Control fouling rates are 1.37 mg/cm²/d and 1.42 mg/cm²/d, respectively.

The dosing regimen used for the 300-mg/L Ca water was 40 mg/L solids high level for 3 days, and 10 mg/L solids for a further 11 days. These results demonstrate the superiority of EPOC as a corrosion inhibitor and scale inhibitor over that of PPMA. In this 300-mg/L Ca water, the PPMA is a poor corrosion inhibitor (0.75 mm/y or 2.96 mpy, and 0.71 mm/y or 2.78 mpy), and gives unacceptable fouling rates (0.274 mg/cm²/day and 0.27 mg/cm²/day).

The EPOC is a good corrosion inhibitor (0.034 mm/y or 1.35 mpy, and 0.046 mm/y or 1.79 mpy), and gave good to very good results on fouling of the heat exchangers at 0.113 mg/cm²/d, and 0.13 mg/cm²/d, respectively.

Treatment Formulation Simplification

The unique property of EPOC in providing both scale and corrosion control performance that would otherwise require the use of two conventional scale and corrosion inhibitors, can be simply demonstrated using bench top aerated jar tests, and rotating coupon corrosion tests.

The synthetic waters used in corrosion

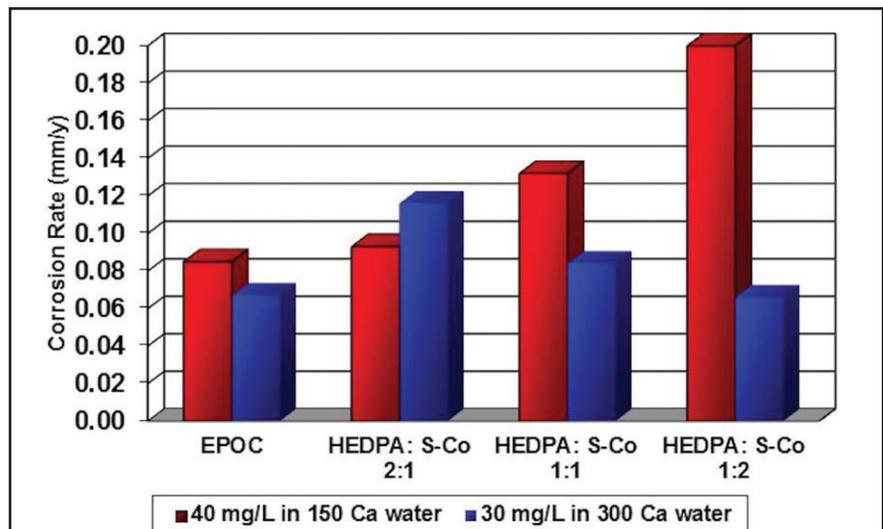


Figure 4. Corrosion inhibitor comparison EPOC versus HEDPA: S-Co formulations dosed as mg/L solids in 150-Ca and 300-Ca waters.

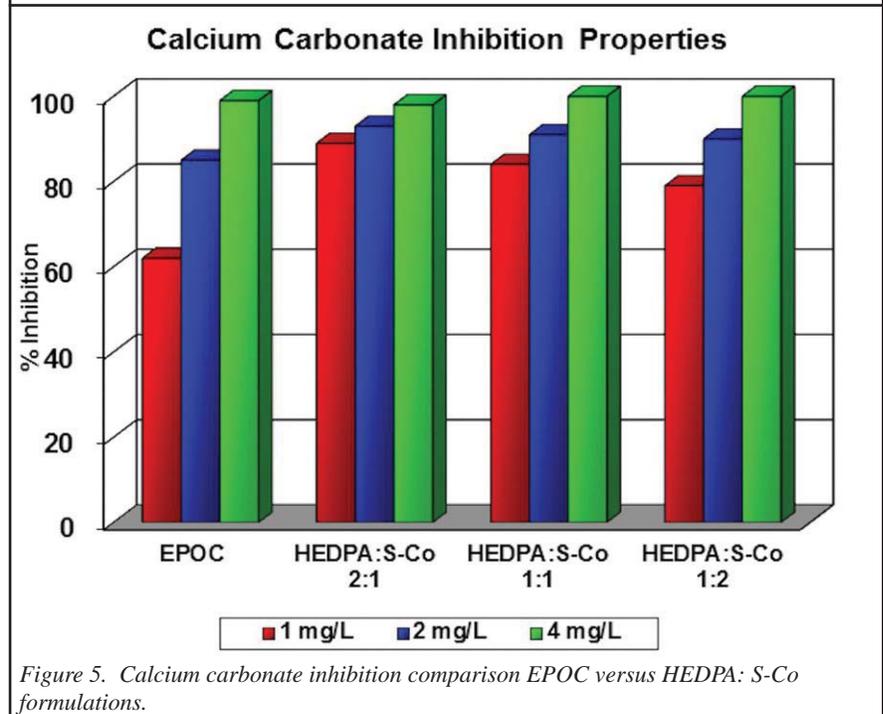


Figure 5. Calcium carbonate inhibition comparison EPOC versus HEDPA: S-Co formulations.

testing are detailed in Table A. This test procedure has been disclosed previously (5). In this rotating coupon corrosion test, a direct comparison of EPOC with 3 different examples of formulated HEDPA and sulfonated copolymer (S-Co) was conducted using beaded finished mild steel coupons. These coupons were pre cleaned and weighed, then rotated in aerated synthetic water for a 42-hour period. The coupons were then removed, and any significant rusting brushed off before cleaning with inhibited hydrochloric acid. After drying, the coupons were

reweighed and corrosion rates calculated from the weight loss, immersion time and surface area.

Corrosion rates are summarized in Figure 4. Control corrosion rates were measured at 0.874 mm/y (34.4 mpy), and 0.523 mm/y (20.58 mpy), respectively in the 150 mg/L Ca, and 300 mg/L Ca waters. Note an increasing corrosion rate with decreasing the HEDPA formulation component in the more aggressive 150 Ca water. This is expected given the corrosivity of this water. The opposite trend is apparent in the higher Ca water,

where an increasing polymer formulation component favors a lower corrosion rate. Corrosion rates with EPOC were found to compare favorably with all 3 formulations, in both waters.

An aerated calcite jar test is designed to rapidly assess the property of an additive to inhibit the precipitation of calcium carbonate (CaCO_3). The water chemistry simulates the cooling water and the high temperature represents the conditions that exist close to a heat exchanger. Air bubbling is used to facilitate carbon dioxide loss, which moves the equilibrium towards carbonate formation, thereby increasing the test severity. The air bubbled solution is heated at 70°C for 30 minutes, after which time the solution is filtered and the calcium remaining in solution determined by EDTA titration. The water conditions are tabulated in Table B. The higher the amount of calcium retained in solution, the greater the scale inhibition properties of the additive.

Figure 5 compares the performance of EPOC versus formulations of HEDPA and S-Co in the same test. At the lowest dose level of 1 mg/L, EPOC calcite inhibition performance is recorded at a modest 60%, compared to the HEDPA : S-Co formulations. However, at 2 mg/L and above, EPOC exhibits equivalent performance compared to all three formulation types, thereby demonstrating EPOC's dual scale and corrosion inhibition functionality.

Cooling Tower Application

Following a decision to eliminate an incumbent phosphonate-manganese corrosion inhibitor and simplify formulations, EPOC was chosen by a water treatment service company and formulator as a direct replacement for use in two recirculating cooling water towers. The key features of these towers, together with observations made during EPOC trials, are summarized below in two case studies.

Fertilizer manufacturing site. Below is an overview of the cooling water facility:

- Feedwater: clarified river water

TABLE B
Calcium Carbonate Scale Test Conditions and Water Chemistry

<i>Component</i>	<i>Reading</i>
Calcium as CaCO_3	375 mg/L
Magnesium as CaCO_3	112 mg/L
Carbonate alkalinity as CaCO_3	85 mg/L
Bicarbonate alkalinity as CaCO_3	440 mg/L
Aeration	500 mL/minute
Duration	30 minutes
Temperature	70°C

- Cycles of concentration: 3-6
- EPOC maintenance dose level: 50 mg/L into the feedwater
- Potential contaminants: high incidence of particulate matter

The pH of the feedwater was 7.5 and in the recirculating water it ranged from 6.5 to 7.5. Total hardness was 20 to 55 mg/L (as CaCO_3) in the feedwater and 100 to 500 mg/L (as CaCO_3) in the recirculating water.

- Calcium hardness (mg/L as CaCO_3): 15-20 in the feedwater, and 92-450 in the recirculating water
- Total alkalinity (mg/L as CaCO_3): 25-45 in the feedwater, and 100-350 in the recirculating water
- Silica (mg/L as silica): 6-18 in the feedwater, and 30-100 in the recirculating water
- Iron (mg/L as Fe^{2+}): 0.1-0.2 in the feedwater, and 0.1 in the recirculating water
- Total dissolved solids (TDS) (mg/L): 65-120 in the feedwater, and 200-700 in the recirculating water
- Suspended solids (mg/L): 3 in the feedwater, and 100-400 in the recirculating water
- Phosphates (mg/L as PO_4^{3-}): 2 in the feedwater, and 20 in the recirculating water

Observations with incumbent corrosion inhibitor. Corrosion rates using the manganese-phosphonate product, dosed as 50 mg/L solids, were 0.064 mm/y (2.5 mpy). Monitoring of mild steel corrosion coupons revealed that inorganic deposits were present, and in deposit-free areas, the mild steel appeared much darker than the initial silver color.

Following switching to EPOC, dosed at the same 50 mg/L as solids, a corrosion rate was measured after 2 months at 0.02 mm/y (0.8 mpy), a reduction of almost 70%. Though inorganic deposits still adhered to the coupons, noticeably less under deposit corrosion was observed.

Tobacco processing site. Below is an overview of the cooling water facility:

- Feedwater: municipal
- Cycles of concentration: 4 to 5
- Corrosion inhibitor maintenance dose level: 40 mg/L into the feedwater

The pH of the feedwater was 7.5 and was 8.1 in the recirculating water. Total hardness was 35 mg/L (as CaCO_3) in the feedwater and 135 mg/L (as CaCO_3) in the recirculating water.

- Calcium hardness (mg/L as CaCO_3): 27 in the feedwater, and 115 in the recirculating water
- Total alkalinity (mg/L as CaCO_3): 14 in the feedwater, and 62 in the recirculating water
- Silica (mg/L as silica): 6 in the

TABLE C
Substitution of EPOC for HPA and Dispersant Components

<i>Component</i>	<i>Formulation 1</i>	<i>EPOC modified formulation</i>	<i>Formulation 2</i>	<i>EPOC modified formulation</i>
Soft water	348	348	356	356
50% caustic soda solution	120	120	60	60
50% zinc chloride solution	6	6	0	0
Tetra potassium pyrophosphate	2	2	0	0
50% PBTC solution	4	4	10	10
HPA	12	0	12	0
44% TTA solution	6	6	16	16
Copolymer dispersant	0	0	20	0
Terpolymer dispersant	22	0	18	0
EPOC	0	34	0	50
Total	520	520	492	492
No. of components	7	6	6	4
Reduction in components		14%		33%

Notes: All components listed as pounds of each ingredient in a 55-gallon drum (Reference 1). Substitution of EPOC for HPA and dispersant components are noted in red.

feedwater, and 31 in the recirculating water

- Iron (mg/L as Fe²⁺): 0.1 in the feedwater, and 0.1 in the recirculating water
- TDS (mg/L): 80 in the feedwater, and 413 in the recirculating water
- Suspended solids (mg/L): 1 in the feedwater, and 20-80 in the recirculating water
- Phosphates (mg/L as PO₄³⁻): 0.5 in the feedwater, and 10 in the recirculating water

Observations with incumbent corrosion inhibitor. Corrosion rates using the manganese-phosphonate product, dosed as 40 mg/L solids, were 0.02 mm/y (0.8 mpy). Surfaces of mild steel corrosion coupons were clean, though much darker than the initial silver color.

Following switching to EPOC, dosed at the same 40 mg/L as solids, a corrosion rate was measured after 2 months at 0.008 mm/y (0.3mpy), a reduction of over 60%.

Cost Reduction

The components of a cooling water formulation can be assembled in many combinations, based on the knowledge and experience of a water treatment supplier. The data presented here show how conventional components can be substituted by EPOC thereby reducing formulation costs. For example, Table C lists the components of two formulations (1). Formulation 1 is proposed for treating a very soft water, with no scaling and with high corrosion potential, whereas Formulation 2 is proposed for treating a very hard water with heavy scaling.

Substitution of HPA and dispersants by EPOC alone in both formulations reduces the number of formulation components by up to 33%, thereby reducing manufacturing complexity. The total cost reduction opportunity available will be the sum of this, together with the wider benefits of streamlined procurement and reduced inventory/working capital.

Summary

This article has sought to show EPOC as an effective option for scale and corrosion inhibition in industrial water

treatment. This treatment approach offers formulators a means of reducing the complexity and cost of existing formulations by substituting their existing corrosion and scale control components with EPOC. ■

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Endnotes

*BWA Water Additives is the water treatment chemical supplier mentioned in the text. The company makes EPOC, or Belcor® 585. The company is focused on discovering and improving water treatment technologies

Author Colin Hogan, Ph.D., is currently technology manager for industrial water treatment at BWA Water Additives in Manchester, U.K. He is involved in new product development and applications research. After holding research and marketing positions at BWA, Dr. Hogan has managed BWA's regional sales teams in both Europe and the Middle East. He holds a doctorate in physical organic chemistry from the University of Liverpool.

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