Development of a Bromine Stabilizer for Outdoor Pools

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Bromine is a popular sanitizer for pools and spas. This popularity is due to the beneficial effects that bromine imparts to the overall swimming experience. Relative to chlorine sanitizers, bromine results in less eye and skin irritation, decreased odor, and reduced bleaching of hair and clothing. Bromine pool sanitation systems may also make the water feel softer, improve pool clarity, and reduce corrosion. The effectiveness of bromine as a primary sanitizer and algicide has not gone unnoticed. Indeed, the benefits of bromine in algae prevention and control has resulted in a number of problem-solving products in the marketplace.

Although bromine provides many benefits and is used extensively in the pool industry, it remains a specialty sanitizer primarily used in spas and indoor pools. This may be due to the fact that effective stabilizers for bromine – i.e., like cyanuric acid for chlorine - are unavailable in the marketplace. Here we describe some of our lab and field studies towards development of such a stabilizer trade named BROMIshield™. We find that this stabilizer dramatically increases bromine residuals by a factor of three or more in outdoor applications when used in conjunction with the Bromitron® Bromine Generator System. The ready availability of this new stabilization technology should prompt increased use of bromine in pools and other outdoor applications.

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Introduction

Bromine can be introduced into pools and spas in several ways and these methods have been reviewed (Duccini 1993, Lowry 1996, Williams 1995). One popular method employs so–called bromine tablets. These slow dissolving tablets are particularly suited for flow–through and erosion feeders and make it relatively simple to maintain a continuous bromine residual for sanitation purposes. Another method requires use of two–part systems based a bromide ion source such as sodium bromide and an activator such as potassium monopersulfate. These systems are particularly suited for spas and typically require manual dosing before and after bathing activity and periodic dosing during periods of inactivity. A third method of introducing bromine involves continuous activation of bromide ion by electricity. This latter approach has much appeal since it easily maintains a continuous bromine residual and limits the handling and storage of irritating or potentially hazardous chemicals.

Units to electrically convert bromide ion to bromine have appeared in the patent literature and several units are available commercially (Lisboa 1995, Atkinson 1989, Howarth *et al.* 1995, Howarth and Dadgar 1991). We chose a Bromitron® Bromine Generator (Bromitron, Inc., Orlando, FL) for this work (Williams *et al.* 1993). This unit consists of several graphite plates arranged in a canister. Rectified current (15V DC) is applied to the plates which causes oxidation of bromide to bromine and formation of hypobromous acid. The pertinent chemistry is shown below:

$$2\,NaBr + 2\,H_2O \longrightarrow Br_2 + 2\,NaOH + H_2 \quad \text{(Electrolysis)}$$
$$Br_2 + H_2O \longrightarrow HOBr + HBr \quad \text{(Hydrolysis)}$$
$$NaBr + 2\,H_2O \longrightarrow HOBr + NaOH + H_2 \quad \text{(Overall)}$$

Overall, one molecule of sodium bromide is converted to one molecule of hypobromous acid. Co– products are sodium hydroxide and hydrogen. Only a small amount of bromide is oxidized to bromine per pass through the unit.

It is well known that sanitizers such as chlorine or bromine can be rapidly depleted upon exposure to heat, sunlight, bather load, bacteria, etc. This places tremendous demands on these sanitizers, particularly during the hot summer months where pool temperatures can rise to 90°F, sunlight exposures can last 14 hours per day or more, and bather loads are high.

The existence of effective stabilization technology for chlorine is the basis for its widespread use in outdoor pools. Without stabilizer, the half–life for loss of chlorine is 12 minutes at pH 8 (Nowell and Hoigné 1992). NSPI guidelines recommend maintaining cyanuric acid levels between 30 and 150 ppm in outdoor pools to mitigate this loss (NSPI 1995). Addition of 25 – 50 ppm cyanuric acid can reduce chlorine consumption by a factor of 2.5 (Unhoch *et al.* 1996).

In the case of bromine sanitizers, effective stabilization technology is unavailable in the marketplace. This lack of a readily available stabilizer for bromine stimulated our interest to develop such a material.

Results and Discussion

Identification of Bromine Stabilization Candidates – Initial Screening Work

Our initial studies focused on identifying whether it was possible to stabilize bromine since it is generally held in the industry that you can't stabilize a bromine pool (Costanzo 1998). We developed an outdoor testing protocol in which stock solutions containing about 4 mg/L bromine were exposed to full sunlight in presence of potential stabilizing agents. For comparison purposes, each run included a bromine control which lacked stabilization agent.

Figure 1 summarizes the results obtained for four different candidates at two different concentration levels. The data are presented in terms of half–life for loss of bromine residual and are normalized by setting the half–life for the control equal to 1. Note that the half–life for the control ranged from 35 to 55 minutes for this series of tests. It is clear that stabilizer D is the best of the group – bromine stability increased by a factor of 16 in the presence of low levels (25 ppm) of this material.

Not all the candidates we tested proved beneficial towards stabilizing bromine. Figure 2 summarizes results with four additional stabilizer candidates. Additives G and H actually promoted bromine loss.

Further Development – Performance in Test Pool

We eventually chose stabilizer A for further development. Although this was not the most effective stabilizer in our screening tests, this was clearly the best overall choice based on several criteria such as cost, availability, performance, physical properties,

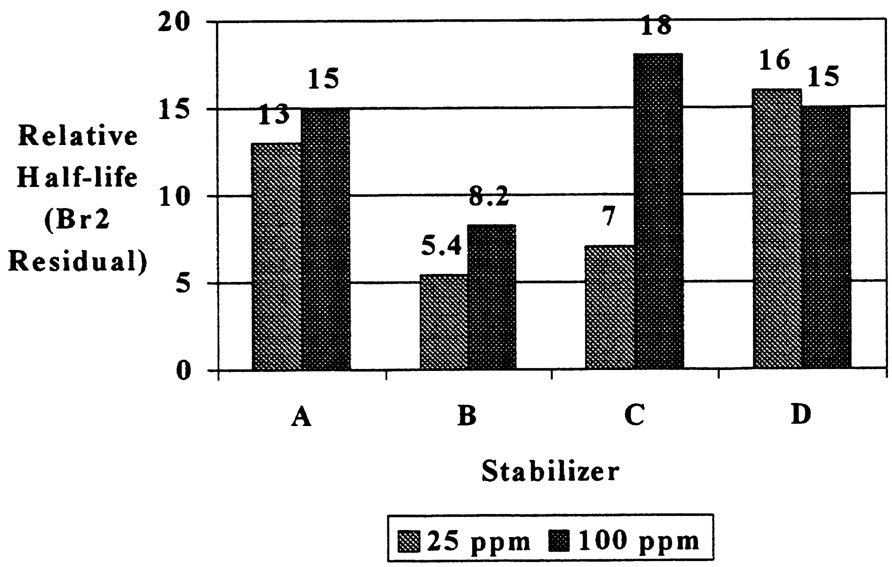

Figure 1 – Bromine Stabilizers: Screening Test Results

Pool size and capacity:	4' (h) x 24' (dia.); 12,000 gallons
Pool location:	Baton Rouge, LA
Sanitation System:	Bromitron Model B–17 Bromine Generator
Weather:	Sunny, high 70s
Pool Temperature:	64 – 70 °F
Pool Chemistry:	pH: 7.6 – 7.8
	Alkalinity: 90 ppm
	Ca Hardness: 140 ppm
	Bromide: 770 ppm
	Chloride: 770 ppm
	TDS (total dissolved solids): 2.0 g/L

Table 1 – Albemarle Test Pool

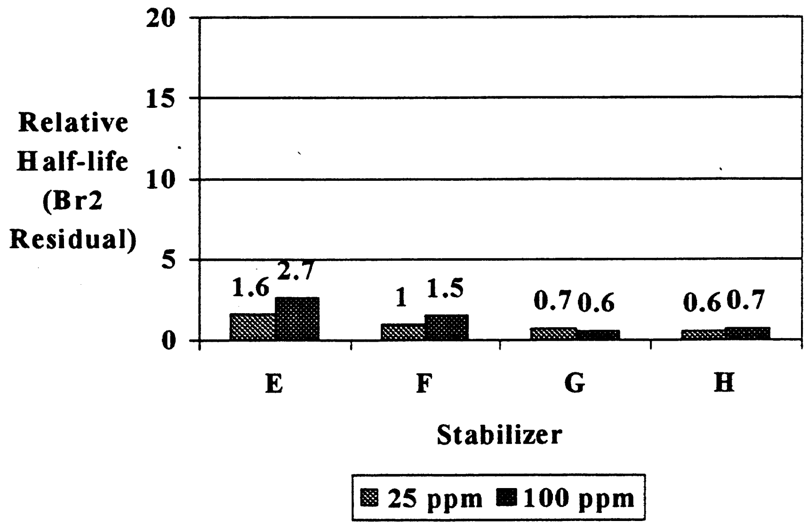

Figure 2 – Bromine Stabilizers: Screening Test Results (continued)

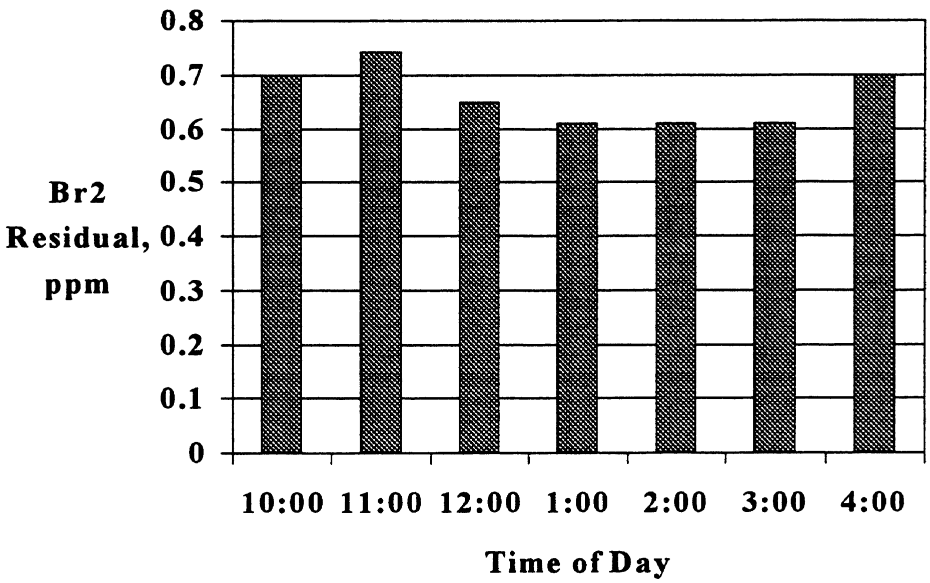

Figure 3 – Bromitron Test Pool: Baseline Data (no stabilizer)

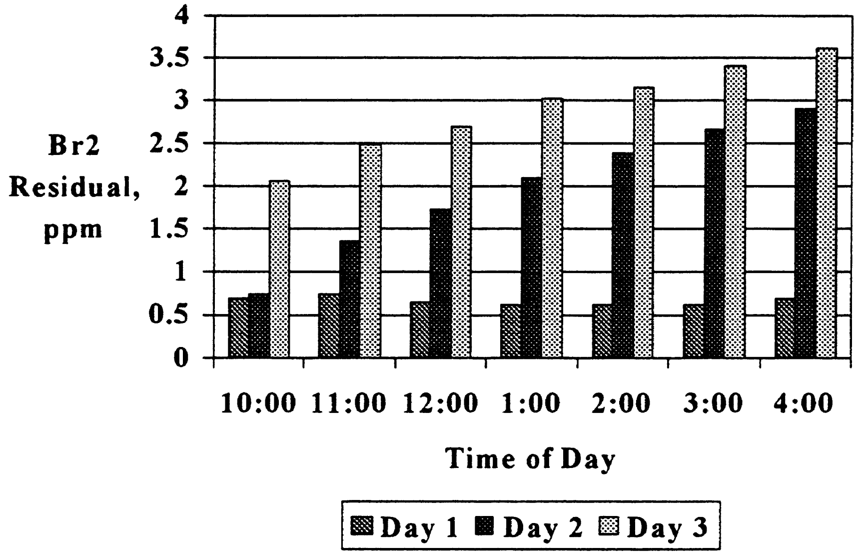

Figure 4 – Bromitron Test Pool: Effect of Stabilizer A (25 ppm Stab. A added at 10:15 am on Day 2)

and toxicology. The compound also appears on the FIFRA list of approved inert materials published by EPA (USEPA 1993).

We studied the performance of stabilizer A in an above ground pool fitted with a Bromitron Bromine Generator located at the Albemarle Technical Center in Baton Rouge, Louisiana. Pertinent data for this field trial is presented in Table 1.

We waited for a period when the weather outlook called for clear, sunny weather for several days. We then commenced a three–day test of Stabilizer A. On day 1, we obtained baseline data by monitoring the pool hourly without added stabilizer (Figure 3). During this period, the bromine generator ran from 10 am to 4 pm and then 10 pm to 4 am (12 hours). On day two, stabilizer A was introduced at 10:15 am (after the 10 am bromine residual reading) and the pool was monitored hourly for an additional two days (Figure 4). Note that due to the high residual readings obtained on the afternoon of day 2, *the overnight bromine generator cycle was eliminated.* The results of this test clearly indicate a significant benefit in maintaining bromine residuals. Use of stabilizer A led to an immediate increase in the daytime bromine residual. The bromine residual by the end of day 3 was 5 times the value obtained in the absence of stabilizer. In addition, the stabilizer minimized overnight loss of bromine.

Final Development – Application at Seasons Resort

We initiated a 5–month trial of stabilizer A at Seasons Resort. Seasons Resort is time–share com-

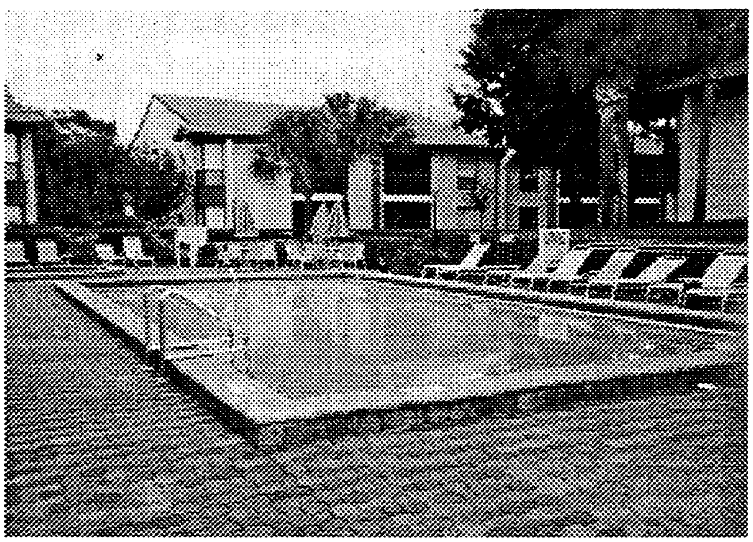

Figure 5 – Pool at Seasons Resort in Orlando, Florida

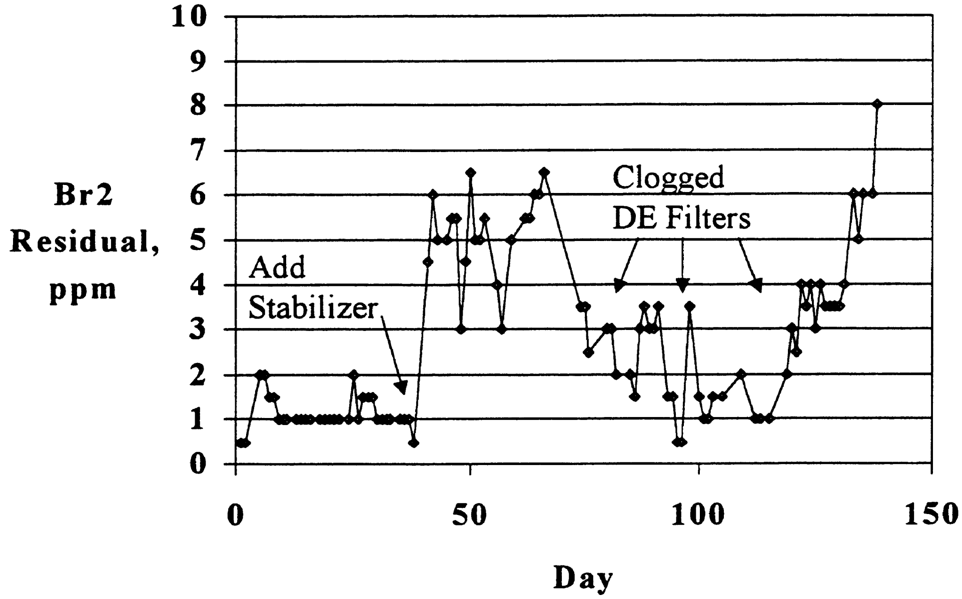

Figure 6 – Seasons Resort: Bromine Residuals

munity located in Orlando, FL. A showcase of the resort is the attractive mauve and grey paved stonework surrounding the 20' x 40' pool. The pool has an overall capacity of 28,500 gallons including a small kiddie pool with an approximate capacity of 850 gallons (Figure 5).

Figure 6 presents the daily bromine residual readings in the pool before and after addition of stabilizer A. As indicated, addition of stabilizer A increased bromine residuals by a factor of 5 or more. This benefit continued to be maintained, more or less throughout the entire study. For a period from early to late August, residuals tended to be low due to problems with the filtration system which caused poor flow through the bromine generator. This problem was corrected and as the more recent data indicate, the pool bromine residual is back to the initial after–stabilizer– addition levels.

In order to maintain adequate stabilizer and bromine levels, additional stabilizer and sodium bromide salt were charged in the pool in mid July and late August. The stabilizer content of the pool and the amount of stabilizer added throughout the entire study are shown in Figure 7. A total of 24 lbs. of stabilizer were added (15 lbs. initially). With the additions, the stabilizer content remained fairly steady at 54 ± 7 ppm and the bromide content of the pool was 1490 ± 190 ppm (Figure 8). Table 2 provides further test details.

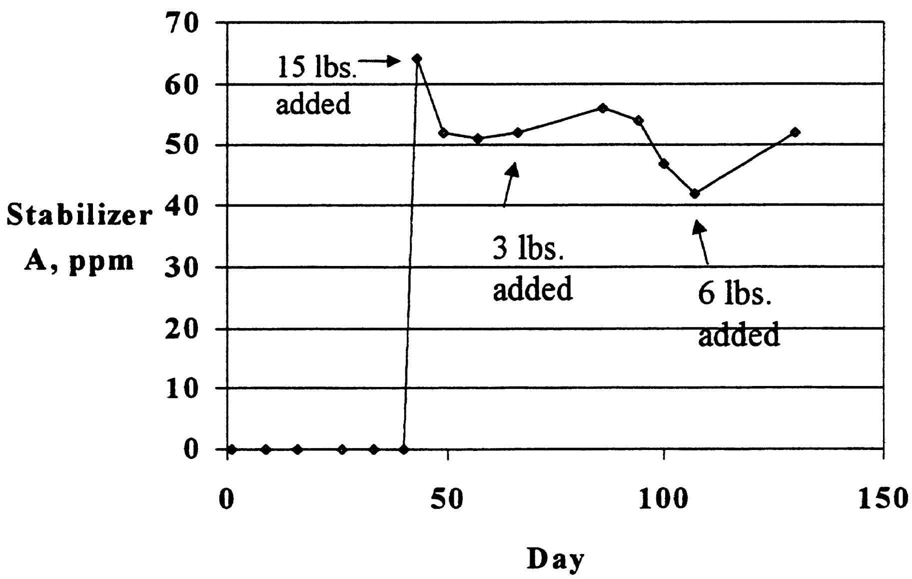

Figure 7 – Seasons Resort: Stabilizer Content

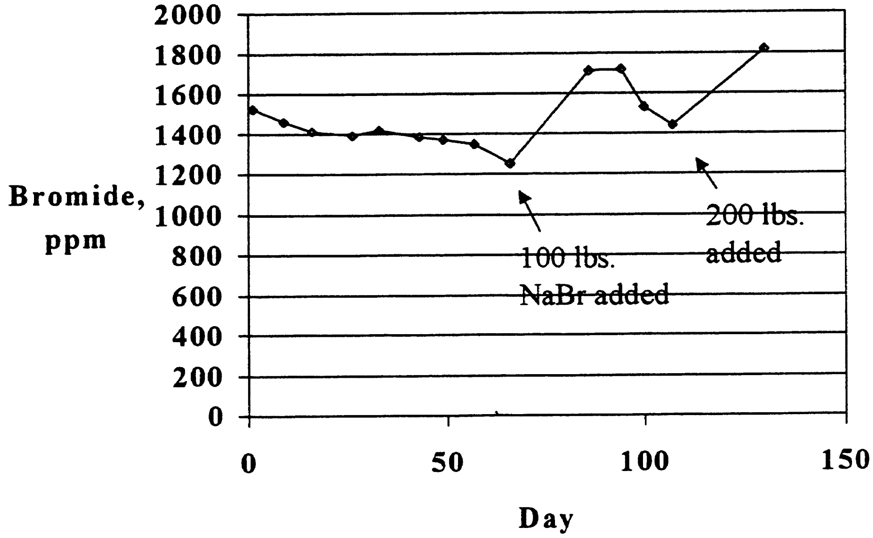

Figure 8 – Seasons Resort: Bromide Level

Sanitation System:	Bromitron Model B–52 Bromine Generator
Pool Temperature:	81 – 88 °F
Pool Chemistry:	pH: 7.8 ± 0.2 units
	Alkalinity: 100 ± 10 ppm
	Ca Hardness: 160 ± 20 ppm
	Bromide: 1490 ± 190 ppm
	Chloride: 160 ± 60 ppm
	TDS: 1.51 ± 0.9 g/L

Table 2 – Seasons Resort Field Trial Summary

Conclusions

We have developed a bromine stabilizer for outdoor pools. Use of this stabilizer increases daytime residuals by a factor of thee or more. The use of this stabilizer should improve the performance and cost effectiveness of bromine sanitation particularly in outdoor applications subjected to high heat, sunlight, and bather loads.

Acknowledgements

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About the Author

Dr. Christopher Nalepa is an R&D Advisor for Albemarle Corporation in Baton Rouge, Louisiana. Chris obtained a Ph.D. in Physical Organic Chemistry from Rice University in 1980. He then joined Ethyl Corporation which spun off Albemarle Corporation as a separate entity in March 1994. During his career at Ethyl/Albemarle, Chris has worked in a number of areas such as development of new curing agents for castable polyurethanes, new UV stabilization packages for polymers, and new halogen and non-halogen flame retardants for polymers. For the past six years, Chris has been investigating the application of bromine-base biocides in industrial and recreational water systems. Chris holds thirteen U.S. patents and has over 40 presentations and publications to his credit.