

Stability of Swimming Pool/Spa Sanitizers:

Comparative Chemical Stability of Polyhexamethylene Biguanide and Hypochlorous Acid

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Proper hygienic conditions in swimming pools and spas are dependent on the maintenance of a minimal level of disinfectant. The two most common disinfectants/sanitizers in residential swimming pools are polyhexamethylene biguanide (PHMB) and chlorine (HOCl). The stabilities of PHMB and HOCl were compared over the range of temperature, pH, organic load, and sunlight that occur in typical pools and spas. The concentration of bioavailable PHMB was unaffected by temperatures between 39°F and 108°F, pH values between 6.2 and 10.0, and organic load. The quantity of the HOCl available for disinfecting purposes was significantly affected by shifts in temperature and pH. In the presence of ammonia HOCl was converted to less active chloramines. PHMB was not depleted under artificial sunlight levels that caused rapid depletion of HOCl. In practical terms, the PHMB concentrations should be monitored weekly and dosed when the active level falls below the recommended level of 6 ppm. The instability of HOCl mandates that testing and adjustments of levels be performed on a daily basis and, depending on which form and feeding system is used, maintained between 3 and 5 ppm.

INTRODUCTION

The two most common chemicals used to maintain hygienic conditions in residential swimming pools are polyhexamethylene biguanide and chlorine. Polyhexamethylene biguanide (PHMB or biguanide) is a stable, highly water soluble, non-oxidizing, cationic polymer that has been used as a swimming pool

sanitizer worldwide for over 15 years. PHMB is commercially available in the United States as Baquacil® Chlorine Free Swimming Pool Sanitizer and Algistat, Softswim® and BaquaSpa™ Sanitizer. PHMB was first introduced as a swimming pool sanitizer in the US in 1983 and for spas in 1993.

The history of chlorine has been well documented. The chlorine products used for treating swimming pools and spas are classified as either unstabilized or stabilized.

Regardless of which chlorine product is used, the chemistry is the same. Chlorine release agents react with water to produce the bioactive hypochlorous acid (HOCl) and less bioactive hypochlorite ion (OCl⁻). Throughout this article HOCl will be used to represent free chlorine. Unstabilized chlorine products are based on inorganic hypochlorite salts of calcium, sodium or lithium. Calcium, sodium and lithium ions are the cationic, or positively charged portion of the hypochlorite salts. All stabilized chlorine products are based on cyanuric acid (CYA), an organic acid. They include sodium dichloro-isocyanurate, potassium dichloroisocyanurate, and sodium trichloro-isocyanurate. The chlorine compounds in this group are referred to as stabilized because when they react with water they form HOCl and CYA, which is used in outdoor pools to stabilize chlorine in the presence of sunlight.

PHMB and HOCl kill microorganisms using quite different mechanisms of action.

PHMB attaches directly to the phospholipids of the cell (cytoplasmic) membrane and results in an irreversible loss of essential cellular components. It was proposed by Fair (1947) that the mechanism of action of HOCl was that of a weak organic acid, in that the uncharged HOCl moiety crossing the cell membrane causes cell death by alteration of the cytoplasmic pH. The charged OCl⁻ is a less effective agent since

charged moieties are able to cross the cytoplasmic membrane only with difficulty. This is only a partially satisfying explanation in that it ignores the non-specific oxidation of essential cellular components that occur on contact with the HOCl molecule. The rates of kill of both PHMB and HOCl under use conditions in pools is similar.

The maintenance of hygienic conditions in pools and spas is dependent on the continuous maintenance of a minimum concentration of sanitizers/disinfectants required to control microbial populations. This minimum concentration of sanitizer/disinfectant needed to control microbial populations is called the minimum inhibitory concentration or MIC. When the concentration of sanitizer/disinfectant falls below the MIC needed, then bacteria, algae, and other microorganisms are able to grow and compromise not only hygienic but also the aesthetic conditions of the pool or spa. The stability of the sanitizer/disinfectant to pH, temperature, organic matter (bather and environmental deposits), and sunlight determines the frequency of monitoring and dosing required by the pool/spa operator. Stabilized chlorine and the use of chemical feeders have reduced the frequency of testing and dosing required by the operator. Sanitizers stable to the elements listed above are also less likely to suffer from sudden rapid depletions and thus expose swimmers to non-hygienic periods between top-up dosages. PHMB and HOCl were comparatively evaluated using simulated pool/spa conditions and historical data.

METHODS

Determination of PHMB and Free Chlorine in Synthetic Pool Water

HOCl was measured using the diethyl-p-phenylene diamine (DPD) colorimetric method 4500-Cl_G (Greenberg 1992). PHMB was assayed using dye binding and quantitated using least squares linear regression of known standards at constant pH. All assays employed a Milton Roy 1001 Plus Spectrophotometer.

Temperature Stability

Synthetic pool water was prepared using deionized, chlorine-demand-free water. The synthetic pool water was balanced according to American National Standards Institute/National Spa and Pool Institute's (ANSI/NSPI) guidelines of total alkalinity of 100–120 ppm and calcium hardness of 190–220 ppm. Sodium bicarbonate and calcium chloride were used to make the necessary adjustments (ANSI/NSPI- 1,6, 1992). After the adjustments for hardness and alkalinity the pH was adjusted to 7.5 ± 0.1 using sodium bisulfate, and the balanced water was divided into two equal portions. PHMB was added to one test sample and calcium hypochlorite was added to the remaining test sample. The PHMB and HOCl were adjusted to

manufacturer's specifications of 10 ppm PHMB (50 ppm Baquacil) and 4 ppm free chlorine (HOCl). Each sample was then sub-divided and stored at 39°F, 79°F, 90°F, and 108°F for 14 days. The temperatures selected represented a range of water temperatures that might be encountered in pools and spas. The PHMB and HOCl concentrations were checked at time of storage and after 3, 6, 10 and 14 days.

The additional HOCl data were obtained from the Handbook of Chlorination (White 1986).

Stability at Various pH's

The pH stability for PHMB was tested at pH 6.2, 8.0 and 10.0, using a citric acid/sodium citrate buffer, boric acid/borax buffer, and sodium carbonate/sodium bicarbonate buffer, respectively (Gomori 1955). Buffered test solutions were prepared using deionized, chlorine-demand-free water. PHMB was added to each of the buffer test solutions to establish the recommended 10 ppm active concentration. The test solutions were stored at room temperature between 74.3°F – 77°F, and the PHMB concentration was assayed at time of storage and throughout the 15 days of storage. These pH values were selected to reflect extremes that could be encountered in pools and spas.

The HOCl data were obtained from the Handbook of Chlorination (White 1986).

Stability in the Presence of Organic Load

Stability of PHMB and unstabilized HOCl was tested in triplicate using 15 gallon tanks of synthetic pool water balanced as above. The water was maintained at 80°F and was circulated and filtered for one hour each day using an aquarium pump and cartridge filter. Calcium hypochlorite was dosed initially to generate 3 ppm of free chlorine, and was topped-up daily to about 3 ppm free available chlorine. The initial PHMB level was 10 ppm, and was supplemented with 28 ppm of hydrogen peroxide to simulate typical pool chemical operating conditions. No additional PHMB or peroxide was added during the study. The tanks were dosed daily with synthetic organic bather load that would represent about 20 bathers for a 10,000 gallon pool using the pool about 1 hour each day. This was equal to 40 pints of perspiration and urine load per day for a 10,000 gallon pool. The synthetic bather load used was that of White (1986) and it contained (mg/L): ammonium sulfate, 161; urea, 277; uric acid, 4; creatinine, 23; creatine, 1; and casamino acids, 57. Samples were taken at T=0, 1, 2, and 24 hours. The samples were assayed for PHMB and HOCl concentrations. The T=0 samples represented a system topped-up with chlorine, but not with the organic load. The samples at one and two hours simulate conditions during use. The 24 hour sample simulated conditions on the day following heavy use and prior to disinfectant top-up.

Photo (Light) Stability

A test solution was prepared using synthetic pool water that contained 50 ppm of PHMB. The solution was transferred to glass vessels, and the volumes were adjusted to result in depths of 1" and 3". These depths were selected because water is a poor transmitter of UV light, and PHMB possess a strong absorbance band in the UV spectrum. Each vessel was sealed with a layer of cellophane film to minimize evaporation. The film had a light absorption of <20% above 310 nm and thus did not inhibit the transmission of light into the water. The test solutions were maintained under constant illumination using artificial lighting that emitted light down to about 310 nm. Controls were maintained in the dark. Samples were taken after 2 and 4 weeks, and were tested for optical density. A decrease in optical density would correlate with a reduction in PHMB concentration. A second study was preformed using test solutions that contained 10 ppm of PHMB. The solutions were exposed continuously to a Xenotest 150 lamp for seven days, which was determined to be equivalent to a month of bright sunlight. UV spectra were taken before and after exposure and used to calculate the amount of decomposition that occurred.

The HOCl data were obtained from the Monsanto Technical Bulletin I-291.

RESULTS AND DISCUSSION

Temperature Stability

The rate of decomposition of HOCl was strongly influenced by increasing temperature. In contrast, there was little correlation observed between change in PHMB concentration versus temperature. The relative temperature stabilities of PHMB and HOCl at temperatures ranging from 39°F to 108°F are shown in Figure 1.

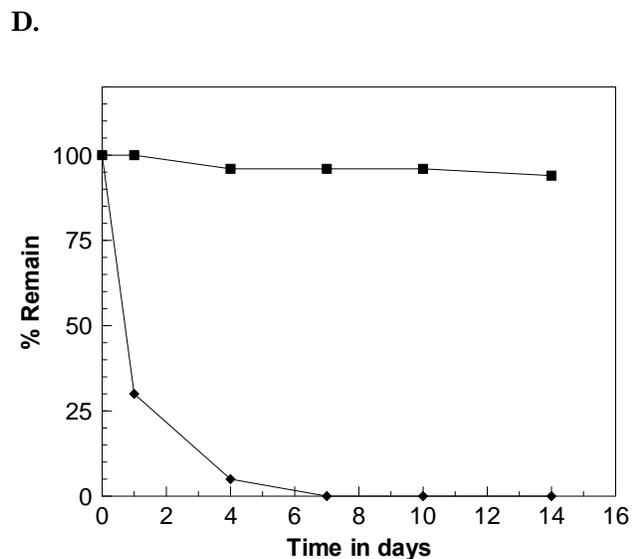
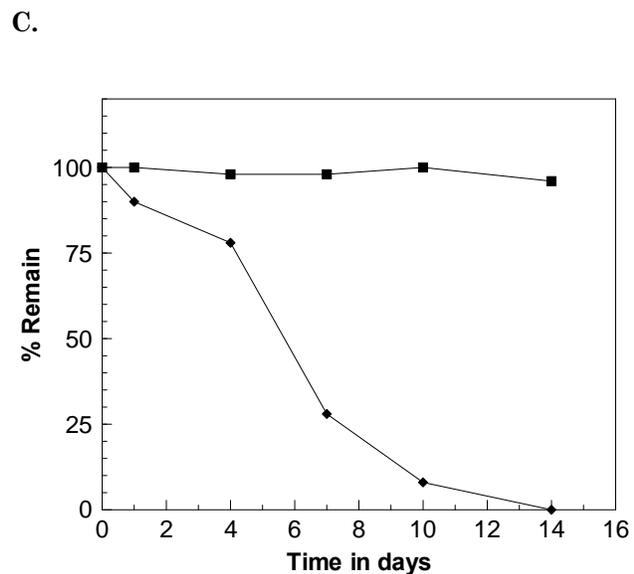
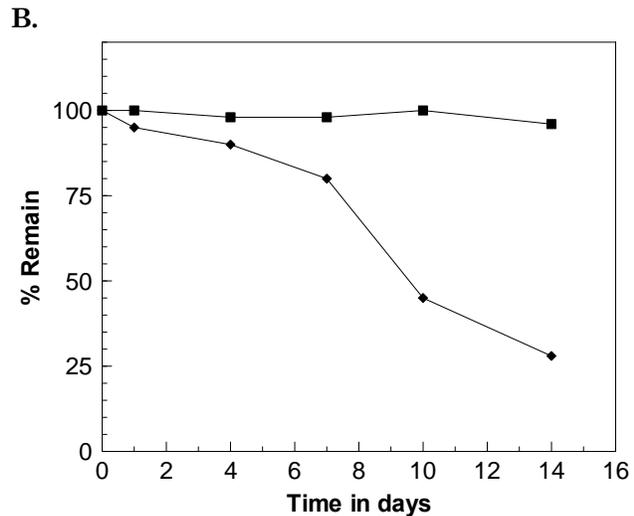
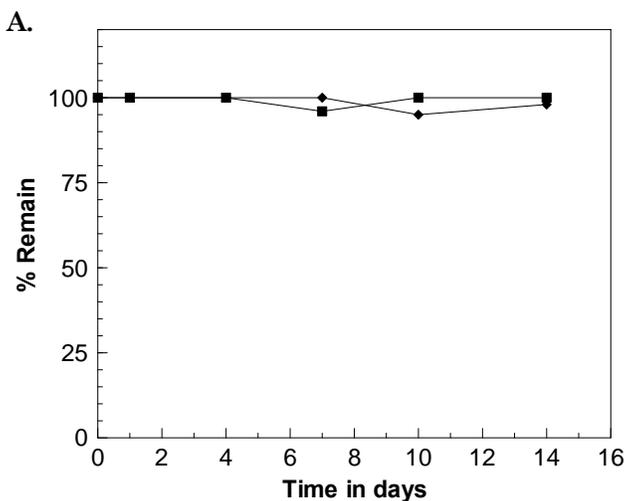


Figure 1 – The relative temperature stabilities of PHMB (■) and HOCl (◆) at various temperatures. A. 39°F B. 79°F C. 90°F D. 108°F

These temperatures represent the full range of temperatures for pool and spa water. At 39°F both PHMB and HOCl were stable. At 108°F temperature and after 14 days of exposure 94% of the PHMB remained. The 108°F temperature is slightly higher than the maximum recommended operating temperature for a spa. This was in sharp contrast to HOCl where 30% of the disinfectant was consumed during the first day, and where none was detectable on day 7. The maintenance of hygienic conditions is dependent upon the maintenance of a proper level of disinfectant in the water. When disinfectant levels fall below the minimal levels, microbial populations may develop in the water column. The temperature stability indicates that the probability of sub-lethal levels of PHMB occurring is low when using a weekly testing regime in pools and spas. The use of HOCl requires much more frequent monitoring and adjustment.

The difference in the relative temperature stabilities of PHMB and HOCl results from their respective chemical structures. This structure of PHMB is shown in Figure 2.

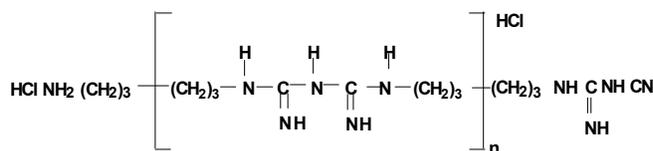


Figure 2 – The chemical structure of PHMB

PHMB is a long chain non-oxidizing polymer and is in a stable form unaffected by pH. The effect of temperature on HOCl concentration is illustrated in Figure 3 (White 1986).

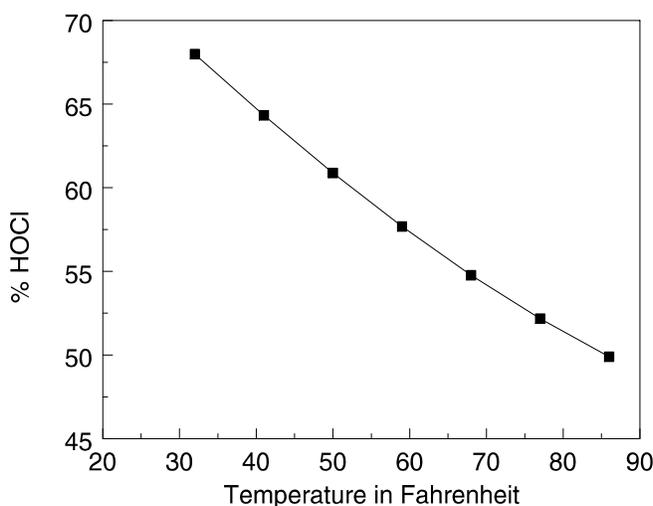


Figure 3 – The effect of temperature on the percentage of HOCl available at pH 7.5

Analysis of the HOCl temperature stability data by linear regression revealed a slope for the curve of -0.34 with a correlation coefficient (r^2) of 0.993 . The slope represents a decrease of 0.34% HOCl per degree Fahrenheit increase. The coefficient indicates that the statistical correlation between temperature and HOCl formation is strong and linear. The HOCl availability curve in Figure 3. is a result of ionization of HOCl in water. When chlorine is hydrolyzed (reacts with water) it disproportionates with the water forming HOCl with a Cl^+ radical and HCl with a Cl^- radical. The chlorine ions in both HOCl and OCl^- are in a $+1$ oxidation state. HOCl is a weak acid that partially dissociates into H^+ and OCl^- . This dissociation equilibrium reaction represented by the equation:

$$K_1 = \frac{(\text{H}^+)(\text{OCl}^-)}{(\text{HOCl})}$$

where K_1 is the ionization constant, (H^+) , (OCl^-) , and (HOCl) are the concentration of the individual ions. K_1 varies with temperature (Morris 1966). The K_1 indicates what percent of the chlorine added to the water is free as the effective disinfectant HOCl and what percent is the less effective OCl^- . In practical terms, a change in pool water temperature from 77°F to 86°F , at pH 7.5, will reduce the amount of HOCl by 3.1% . Although this is insignificant for swimming pools it has very significant implications for spas where water temperature is maintained between 100°F and 104°F . The equilibrium is also important in superchlorination. The amount of HOCl present at an average pool operating temperature of 86°F , and pH 7.5, is only about 50% of the total chlorine in the system. During superchlorination a dose of one pound of one pound of calcium hypochlorite (65% available chlorine) in a 10,000 gallon pool will generate only 3.9 ppm HOCl, at pH 7.5. To achieve superchlorination levels of chlorine (8 ppm HOCl) a dose of two pounds of calcium hypochlorite is required rather than the recommended one pound dose.

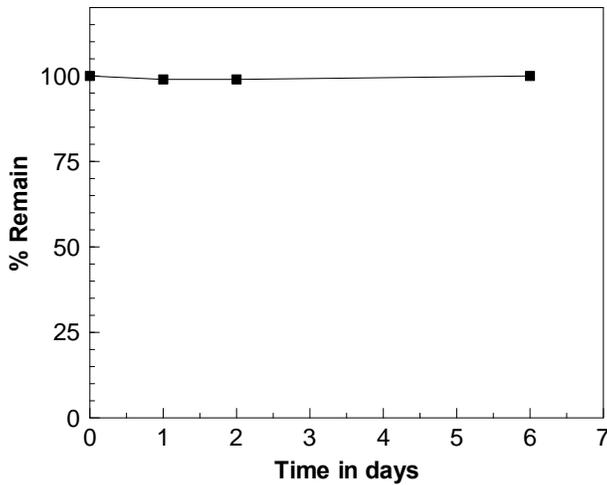
pH Effect

The evaluation of PHMB and HOCl stability to pH changes revealed a pattern similar to that seen with temperature. The relative pH stability of PHMB at pH values of 6.2, 8.0, and 10.0 are shown in Figure 4. At all three pH values no loss of PHMB assay was observed over the six days of storage at pH 6.2 and the 15 days of storage at pH 8.0 and 10.0, at ambient temperatures ($74.3^\circ\text{F} - 77^\circ\text{F}$). PHMB is stable over the range of pH values for pools and spas. Changes in pH affect the concentration of HOCl in the water through the K_1 shown above. As the pH increases the amount of HOCl decreases, shifting the equilibrium toward

the less active OCl^- moiety. This is illustrated in Figure 5 (White 1986). Analysis of the data by linear regression showed a slope of -47.8 and a correlation

spas is influenced by chemical treatments and will drift toward more basic pH because of the large amount of air introduced to the water from operation of the blowers.

A.



B.

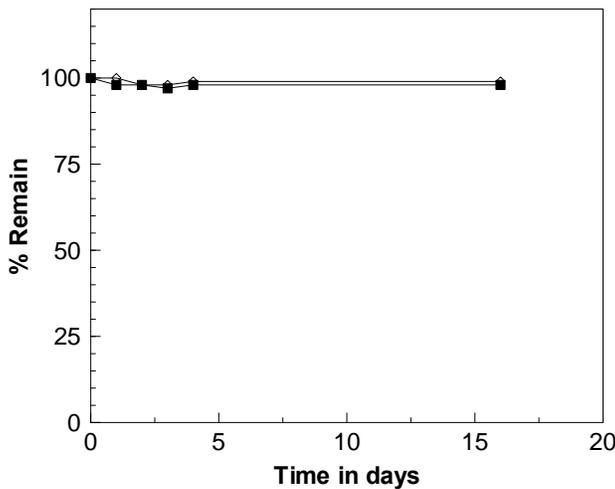


Figure 4 – The stability of PHMB (■) at various pH values A. pH 6.2, B. pH 8.0 (■) and pH 10.0 (◇)

coefficient of 0.993. The slope shows that for every increase of 0.1 pH unit the HOCl concentration was reduced by 4.8%. For disinfection purposes, as pH increases, the amount of chlorine needed to generate similar amounts of HOCl significantly increases. A shift in pH from 7.0 to 8.0 at 86°F would decrease the HOCl by 48%. The change in HOCl for the more narrow recommended range of 7.4–7.6 was 9.6%. The magnitude of this effect is not as significant for pools as it is for spas because spas operate at higher average temperatures and pH values. The operating pH for

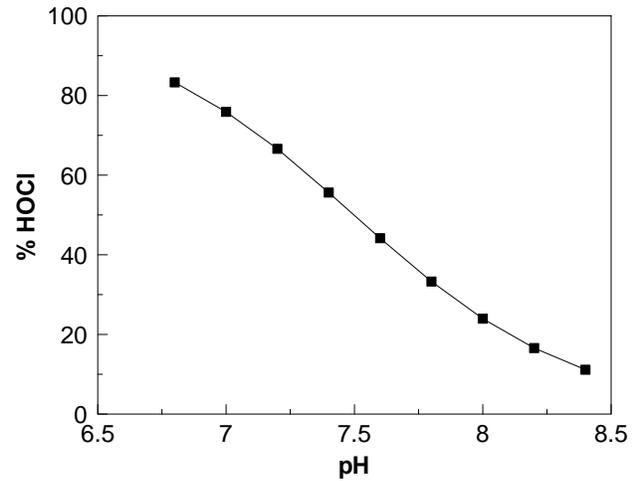


Figure 5 – pH effect on HOCl Concentration at 86°F

Stability in the Presence of Organic Load

The relative consumption rates for PHMB and HOCl were plotted versus time in Figure 6. Time qualitatively represents amount of bather load because bather load additions were made daily. Consumption rates of sanitizers/disinfectants were used to quantify the effect of organic load on performance. The consumption rates were calculated using linear regression analysis of the hourly sample data. The

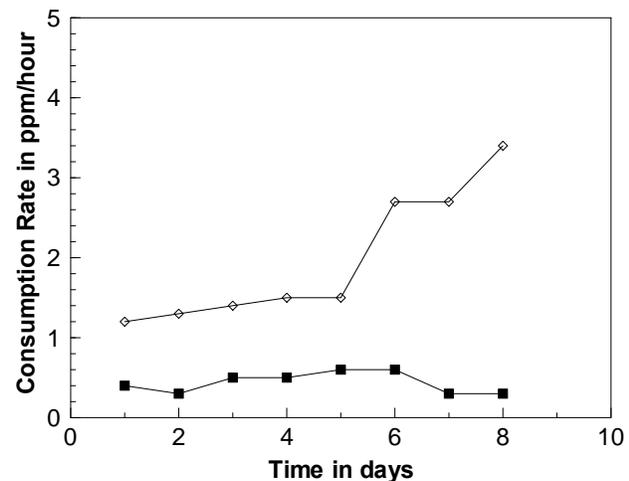


Figure 6 – The average hourly consumption rates of PHMB (■) and HOCl (◇) for each day during the test period. The days correlate with the bather load additions

average consumption rate for PHMB was 0.4 ± 0.2 ppm/hour. The standard deviation showed that the consumption rate was constant throughout the test and that the PHMB concentration was constant and unaffected by increasing organic load levels.

The average consumption rate for HOCl was 1.9 ± 0.8 ppm/hour. The larger standard deviation indicates that the consumption rate was not constant over the test period and thus less stable to increasing organic load levels. The consumption rate was constant at 1.4 ± 0.1 ppm/hour for the first five days, but significantly increased from day 6 through the end of the test. These data show that the consumption rate for PHMB is unaffected by the daily accumulation of organic materials, but that HOCl is depleted over time by the accumulation of organic materials.

A partial explanation for the consumption rates of PHMB and HOCl in pools and spas is their reactivity with organic debris in the pool/spa water column. PHMB reacts preferentially with proteins and fatty acids found in the bacterial membrane, and only slightly with other organic compounds found in pool/spa water. HOCl reacts non-specifically with all organic compounds as well as with ammonia to produce by-products containing combined chlorine or chloramines. Chloramines are less effective disinfectants than HOCl and are undesirable because they contribute to skin and eye irritations and odors in pools and spas. This is why it is recommended to test for combined chlorine, and to superchlorinate when the combined chlorine reaches or exceeds 0.2 ppm (ANSI/NSPI-1, 1992). The superchlorinating dose is ten times the amount of combined chlorine level. It is also recommended that the superchlorination frequency be every other week except when the water temperature exceeds 85°F then the frequency changes to weekly. For spas it is recommended that the spa be shocked on a daily basis using ten times the amount of combined chlorine level (ANSI/NSPI-6, 1992). Because PHMB does not react with common pool and spa organic compounds an oxidizer is needed to assist in controlling their accumulation. The preferred oxidizers for use with PHMB are peroxides, peracids, and perborates. PHMB in conjunction with ozone can also be used to control the accumulation of organics in pool and spa water. Chlorine and bromine cannot be used because they react with the PHMB, removing it from the water as a sticky yellow precipitate.

The stability of a disinfectant to organic load is important because pools and spas are open systems where nitrogenous or carbonaceous compounds including perspiration, urine, proteins, skin cells, personal care products, leaves, dirt, and grass are able enter the water. The sanitizers/disinfectants purpose is to control microorganisms including pathogenic and nonpathogenic bacteria, algae and fungi. If the sani-

tizer/disinfectant is consumed by the interaction with the organic load, then more will be required to control the microorganisms. The amount of organic load used in this study was heavy and simulated that seen in commercial pools with a daily use equivalent to 20 swimmers in a 10,000 gallon pool. This load could also represent one bather in a 500 gallon spa.

Photo (Light) Stability

The PHMB photo stability is shown in Figure 7. Vessels of both 1" and 3" depths, containing PHMB exposed to artificial sunlight, demonstrated similar stabilities to those stored in the dark. A slight increase in optical density was observed as a result of evaporation. This was more pronounced in the four week samples and the one inch depth tank. The PHMB exhibited excellent stability to the simulated sunlight. Samples exposed continuously to a Xenotest 150 lamp retained 90% of PHMB after seven days. Exposure of this condition simulated one month of bright sunlight. PHMB is considered stable in the presence of sunlight.

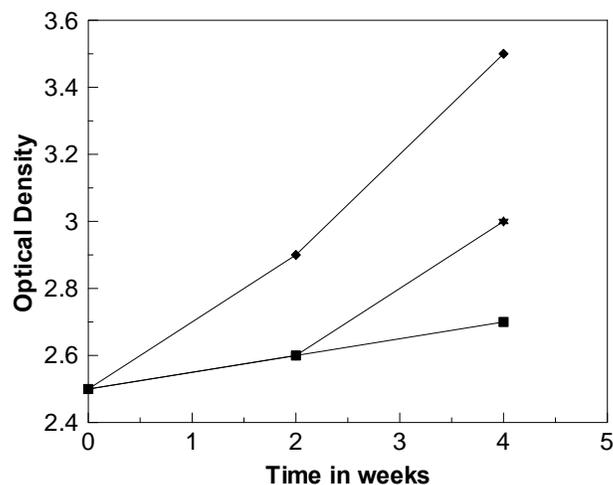


Figure 7 – The stability of PHMB in the presence of artificial sunlight. 1" deep vessels (♦), 3" deep vessels (★), and control vessels stored in the dark (■)

The effect of sunlight on HOCl was documented by Monsanto in their Technical Bulletin I-291, "How Monsanto Cyanuric Acid Stabilizes Chlorine In Swimming Pools and Helps Reduce Disinfection Costs." The correlation between HOCl consumption and CYA level is illustrated in Figure 8. Monsanto's data showed that 90% of the HOCl in pool water was consumed in 2-3 hours on a sunny day. The addition of 25 ppm CYA significantly improved HOCl stability to sunlight and reduced the consumption rate by 2.5 times. Therefore, after the addition of 25 ppm CYA, HOCl was consumed in 7.5 hours rather than 2-3 hours. Increasing

the CYA to 50 ppm yielded only a slight improvement in the consumption rate. The stability of HOCl to sunlight is based on the chlorine atom's electronic structure. The chlorine atom's most stable state is as the Cl⁻ radical rather than a Cl⁺. Therefore, the positively charged chlorine radical is more reactive and will be readily reduced to the negatively charged ion when exposed to sunlight.

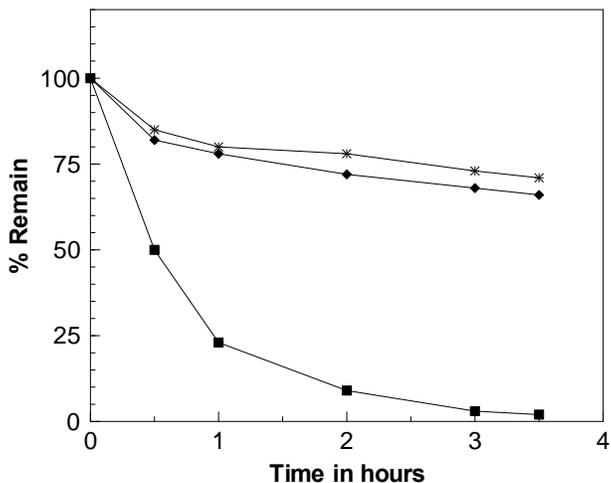


Figure 8 – The effect of cyanuric acid levels of 0 ppm (■), 25 ppm (◆), and 50 ppm (*) on the stability of chlorine in pool water exposed to sunlight

SUMMARY AND CONCLUSIONS

PHMB was unaffected by varying temperatures, pH values, organic load, and sunlight; whereas the HOCl concentrations were affected by increasing temperature, pH, organic load, and exposure to sunlight. This difference is attributed to the structures and the reactivity of the compounds in water. PHMB is a non-oxidizing polymer that does not dissociate in water. PHMB kills microbes by disrupting the cell integrity and interacting with proteins on the cell surface. It is relatively unreactive with organic compounds common in pool and spa environments. Because PHMB is non-oxidizing it is recommended that pools and spas using PHMB include an oxidizer such as hydrogen peroxide to remove accumulated organic debris in the water column. Chlorine forms HOCl and OCl⁻ when dissolved in water. This is an equilibrium reaction that is effected by temperature and pH. As the temperature and pH increase, the equilibrium shifts in favor of OCl⁻, decreasing the concentration of the bioactive HOCl. HOCl is unstable and reacts with ammonia to form less bioactive chloramines. HOCl is also depleted by the photo-oxidation of sunlight which is why CYA is used in swimming pools.

PHMB and chlorine products have a long histories of successful use in swimming pools and spas as sanitizers/disinfectants. The stability of the sanitizer/disinfectant to temperature, pH, organic load, and sunlight determines the frequency required for testing and product addition. This has no effect on microbial control if proper levels are maintained, but rather a convenience to the pool and spa owner/operator. Historical data have shown that the need to test and dose PHMB in residential pools and spas varies, but on average should be completed on a weekly basis. HOCl must be monitored on a daily basis to prevent depletion and possible uncontrolled microbial growth. Under identical conditions of combined depletion by temperature, pH, bather use and sunlight, HOCl is significantly less stable than PHMB. The reduction in daily monitoring makes PHMB more convenient to use than chlorine.

References

- American National Standard for Public Swimming Pools, NSPI, pp. 58–9 (1992).
- American National Standard for Residential Portable Spas, NSPI, pp. 28–9 (1992).
- Fair, G. M., J. C. Morris, and S. L. Chang. "The Dynamics of Water Chlorination." *Journal of the New England Water Works Association* 61, 285 (1947).
- Gomori, G. "Preparation of Buffers to Use in Enzyme Studies." *Methods in Enzymology* 1, 138–146 (1955).
- Greenberg, A. E., L. S. Clesceri, and A. D. Eaton. *Standard Methods For The Examination Of Water and Wastewater. (APHA, AWWA, and WEF) 18th Edition*, pp.4–45 to 4–46 (1992).
- Monsanto Technical Bulletin I–291, "How Monsanto Cyanuric Acid Stabilizes Chlorine In Swimming Pools And Helps Reduce Disinfection Costs." 45.
- Morris, J. C. "The Acid Ionization Constant of HOCl from 5 to 35°C." *Journal of Physical Chemistry* 70, 3798 (Dec. 1966).
- White, G. C. *Handbook of Chlorination*. Van Nostrand and Reinhold, p. 479, (1972).
- White, G. C. *Handbook of Chlorination*. Van Nostrand and Reinhold, Second Edition, pp. 155, (1986).

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Peter S.K. Lee, Ph.D. is currently the Senior Development Biologist with Zeneca Pool Products. He is the author and co-author of many technical papers, and has received specialized training in many fields including air quality and industrial water process treatment. He is particularly interested and involved in microbiological risk assessment, and the development, evaluation, and application of disinfectants and algaecides for swimming pool and spa use.