

# Effect of Recreational Water Sanitizers on Swimwear

## Comparative Effect of Polyhexamethylene Biguanide and Chlorinated Pool Water on Swimwear

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Pool water treatment chemicals and sunlight exposure are two key factors that influence the colorfastness and physical degradation of swimwear fabrics. Two commonly used pool water disinfectants are chlorine and polyhexamethylene biguanide (PHMB). Polyhexamethylene biguanide is the only non-halogen based sanitizer registered by the EPA for recreational water. PHMB is a stable, highly water soluble, non-oxidizing, cationic polymer that is used in conjunction with hydrogen peroxide as an oxidizer and an alkyl dimethyl benzyl ammonium chloride as an algicide. The PHMB system has been used to treat swimming pools worldwide for over 15 years.

The effects of balanced synthetic pool water, chlorine treated pool water, and PHMB/hydrogen peroxide/quaternary ammonium treated pool water on color and burst strength of three knitted swimwear fabrics were investigated. These three treatments were evaluated in the presence and absence of artificial sunlight. The greatest color change and reduction in burst strength was exhibited by exposure to light with no chemical treatment. Chlorine treated pool water had the greatest effect on color change and reduction in burst strength for the chemical treatments. The PHMB/hydrogen peroxide/quaternary ammonium treated pool water had no greater impact on color change or reduction in burst strength than the balanced synthetic pool water control. As a general rule, swimwear life may be extended by drying in indirect light.

## INTRODUCTION

Consumers take time and great pride in selecting the perfect style of swimwear to suit their needs. Historically, this swimwear had a limited use period due to exposure to sunlight and the recreational water treatment chemicals used. Color fading or loss of fabric integrity and strength are two concerns for swimwear. Swimwear as well as dye and fabric manufacturers have attempted to combat this situation for many years. (Perenich, 1991) Swimming pools are treated to control undesirable microorganisms with either chlorine products or with a non-chlorine system based on polyhexamethylene biguanide (PHMB or biguanide).

All chlorine products used for treating recreational waters are based on the release and maintenance of free chlorine as hypochlorous acid (HOCl). HOCl is a strong oxidizer that is used in recreational water at 2 to 5 ppm to control the growth of bacteria and algae. HOCl has also been associated with the bleaching and degradation of swimwear fabric (Epps, 1987) and vinyl pool liners and covers. (Francey and Giesner, 1989) Household laundry bleaches sold in the U.S. contain 5.25% (52,500 ppm) HOCl and are noted for their ability to bleach non-colored safe fabrics. HOCl is used in laundry applications at approximately 180 ppm.

The only non-halogen based sanitizer registered by the EPA for recreational water use is PHMB. PHMB 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. PHMB is used in swimming pools and spas at a concentration

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between 6 and 10 ppm. In PHMB treatments, hydrogen peroxide is used as an oxidizer at concentrations between 0 and 27.5 ppm and algal control is maintained by alkyl dimethyl benzyl ammonium chloride (QAC or quats) at a concentration of 2 to 2.5 ppm.

The objective of this research was to compare the effects of chlorinated and PHMB system treated swimming pool water on the colorfastness and integrity of swimwear fabric.

## MATERIALS AND METHODS

### Fabrics

Swimwear fabrics and colors evaluated were: fabric A, 46% polyester, 46% cotton and 8% lycra spandex blend – medium blue; fabric B, 85% nylon plus 15% lycra spandex blend – chartreuse; and fabric C, 100% nylon – bright pink. Samples from each fabric were cut into 4.25 inch x 4.25 inch swatches. All exposure studies were conducted in triplicate.

### Balanced Synthetic Pool Water and Chemical Treatments

Balanced synthetic pool water (SPW) was prepared using demineralized water. The 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, 1992). After the adjustment for hardness and alkalinity, the pH was adjusted to  $7.5 \pm 0.1$  using sodium bisulfate.

Three different PHMB plus SPW solutions were prepared using the balanced pool water as shown in Table 1.

PHMB was assayed using dye binding and quantified using least squares linear regression of known standards at constant pH. PHMB assays employed a Baquacil ProLab colorimeter model STC-K. Solutions 1 and 2 above were selected to represent the range of typical levels found in pools. In normal pool operation hydrogen peroxide is added monthly at a dose of 27.5

ppm active. Solution 3 was selected as a 2X use level for evaluation purposes only. The EPA approved use directions specify that PHMB levels be maintained in recreational waters at between 6 and 10 ppm. The use of levels above 10 ppm PHMB is not recommended and is a violation of the EPA approved product label.

Three calcium hypochlorite treated SPW solutions of 2 ppm, 5 ppm, and 10 ppm free chlorine were prepared using the balanced pool water. HOCl was measured by the diethyl-p-phenylene diamine (DPD) colorimetric method 4500-Cl G (Greenberg et al, 1992) using a Baquacil ProLab colorimeter model STC-K. The concentrations of 2 and 5 ppm HOCl represent recommended daily maintenance levels and the 10 ppm level is used during superchlorination. Bathing during periods of superchlorination is not recommended.

### Chemical Exposure Conditions

Fabric exposures employed a Launderometer apparatus and American Association of Textile Colorist and Chemists (AATCC) Test Method 61–1989. The fabric specimens were placed in a Launderometer canister with 200 ml of test water. The Launderometer cycle temperature was 70°F and the cycle time was 45 minutes for Synthetic Pool Water and 60 minutes for PHMB and chlorine. Upon completion of each run the fabrics were removed from the canister to air dried in a darkened room maintained at  $70 \pm 2^\circ\text{F}$  and  $65 \pm 2\%$  RH.

### Light Exposure

Light treatment to simulate outdoor exposure to sunlight was based on ANSI/ASTM Method G53–77. A QUV Accelerated Weathering Tester with UVA–340 lamps was used to simulate sunlight exposure. All the treated fabric samples were exposed to continuous light at  $145 \pm 5^\circ\text{F}$  for the equivalent of 40 AFU's. This exposure protocol was determined by the color change of AATCC blue wool reference fabric. The exposure cycle was 10 hours. Following exposure the fabrics were conditioned for 24 hours.

Component	PHMB POOL WATER SOLUTIONS		
	1	2	3
PHMB (ppm)	5	10	20
Hydrogen Peroxide (ppm)	13.75	27.5	55
QAC (ppm)	2.5	2.5	2.5

Table 1 – PHMB Pool Water Solutions



## Determination of Color Change ( $\Delta E$ CIELAB)

Color readings and calculations were made using a Hunterlab Tristimulus Colorimeter® D-25-M-9. A minimum of five readings were made per sample, for each fabric, and mean  $\Delta E$  values were calculated from the three specimen values. The values were calculated from the differences in L, a, and b readings between untreated and treated samples using the following equation:

$$\Delta E (\text{CIELAB}) = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

L, a, b readings describe the color of the fabric where "L" represents a light to dark measurement (+ $\Delta L$  is lighter and - $\Delta L$  is darker in color intensity), "a" represents the red to green color component (+ $\Delta a$  indicates a more red or less green component, and - $\Delta a$  indicates a less red or more green color component), and "b" represents yellow to blue color component (+ $\Delta b$  indicates a more yellow or less blue color component, and - $\Delta b$  indicates a less yellow or more blue color component).

## Determination of Fabric Burst Strength

Burst strength for each fabric was determined using ASTM Method D3786-87. Unexposed fabric controls were used to determine change in burst strengths from treated samples. Burst strength was tested in triplicate and the average percent change was calculated.

## RESULTS AND DISCUSSION

### The Effect of Chemical and QUV Exposure on Color Change ( $\Delta E$ CIELAB)

Figure 1 illustrates the effect of SPW, HOCl, and PHMB systems on the colorfastness of the fabric in the absence of light. The  $\Delta E$  data from the PHMB systems representing 5 and 10 ppm treatments and the HOCl concentrations of 2 and 5 ppm treatments were combined, respectively. The combination of these exposure ranges reflects common exposure ranges in swimming pools. The HOCl had a significant effect on the colorfastness of the dye used on fabric A. In contrast, the PHMB system had no greater effect than that of the water control on fabric A. HOCl treatment of fabric C resulted in statistically significant color loss ( $\Delta E = 2.40 \pm 0.51$ ). There was no statistical difference between the PHMB system ( $\Delta E = 1.33 \pm 0.39$ ) and the water control ( $\Delta E = 1.23 \pm 0.38$ ). There was no difference in  $\Delta E$  for any of the treatments on fabrics B.

Figures 2 and 3 illustrate the effect of increasing concentrations of HOCl and the PHMB system, respectively, on colorfastness of the fabric in the absence of light. Fabrics A and C displayed statistically significant dose related color losses during exposure to HOCl. The R-square values for HOCl to color loss were 0.960 and 0.951, respectively. Fabrics exposed to the PHMB system displayed no significant color loss regardless of chemical exposure level. These results were not unexpected in that PHMB is a non-oxidizing polymer and hydrogen peroxide is a weak oxidizer. Hydrogen peroxide used in the PHMB system has an

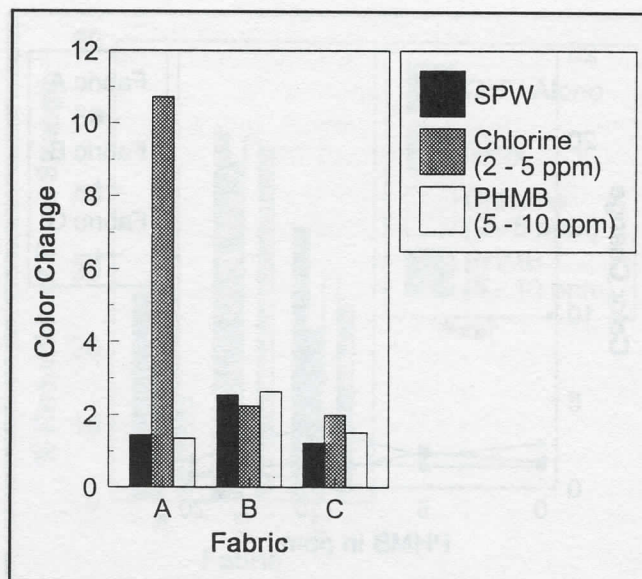


Figure 1 - Effect of Synthetic Pool Water, HOCl, and PHMB system on color change ( $\Delta E$ ) for three fabrics in the absence of light. Average  $\Delta E$  values from the HOCl 2 and 5 ppm treatments and the PHMB systems 5 and 10 ppm treatments were combined, respectively.

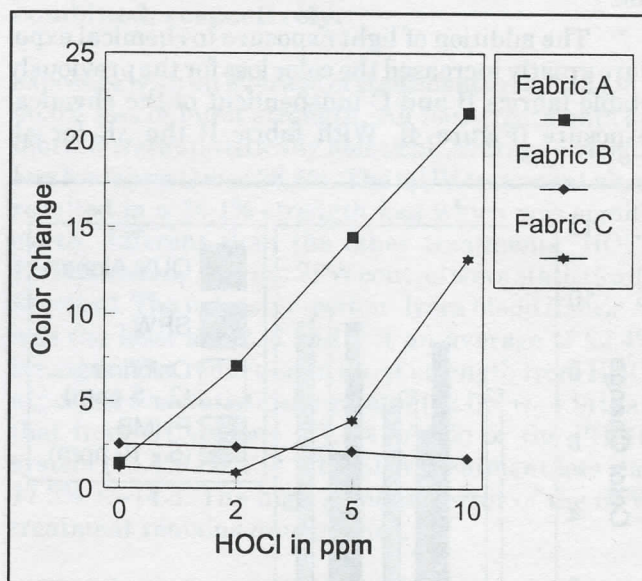
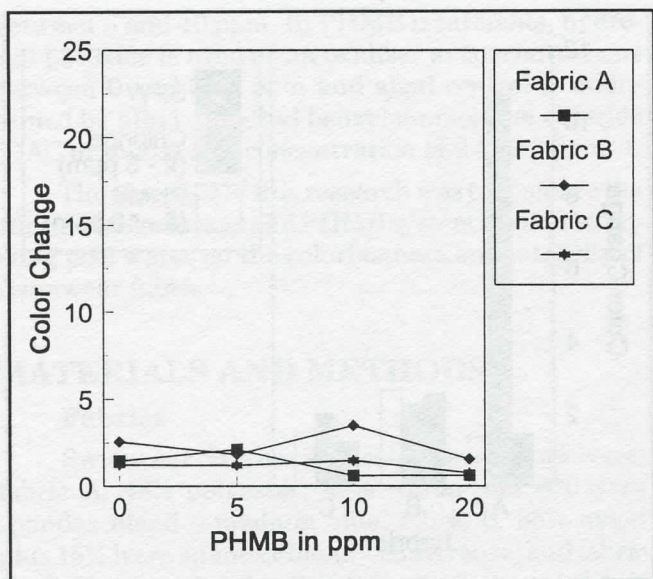


Figure 2. Effect of increasing concentrations of HOCl on the color change ( $\Delta E$ ) for three fabrics in the absence of light.

cant dose related color losses during exposure to HOCl. The R-square values for HOCl to color loss were 0.960 and 0.951, respectively. Fabrics exposed to the PHMB system displayed no significant color loss regardless of chemical exposure level. These results were not unexpected in that PHMB is a non-oxidizing polymer and hydrogen peroxide is a weak oxidizer. Hydrogen peroxide used in the PHMB system has an

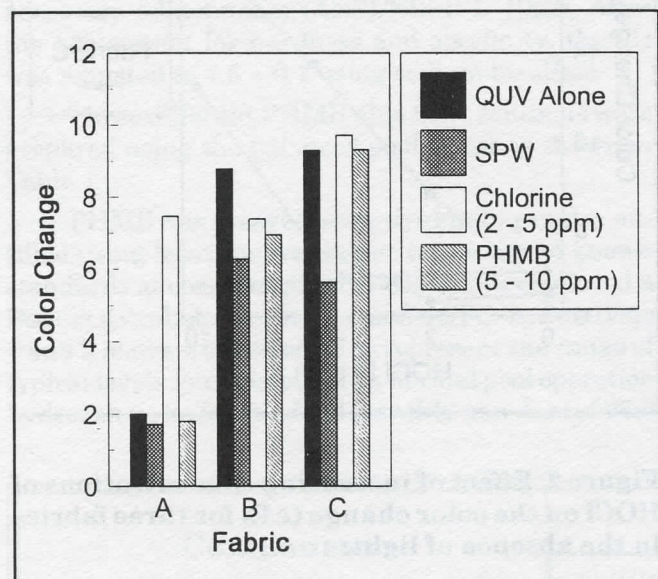




**Figure 3. Effect of increasing concentrations of the PHMB system on the color change ( $\Delta E$ ) for three fabrics in the absence of light.**

oxidation potential of  $-0.68v$ ; whereas,  $HOCl$  is commonly used as a bleaching agent and has an oxidation potential of  $-1.63v$ , considerably stronger than peroxide.

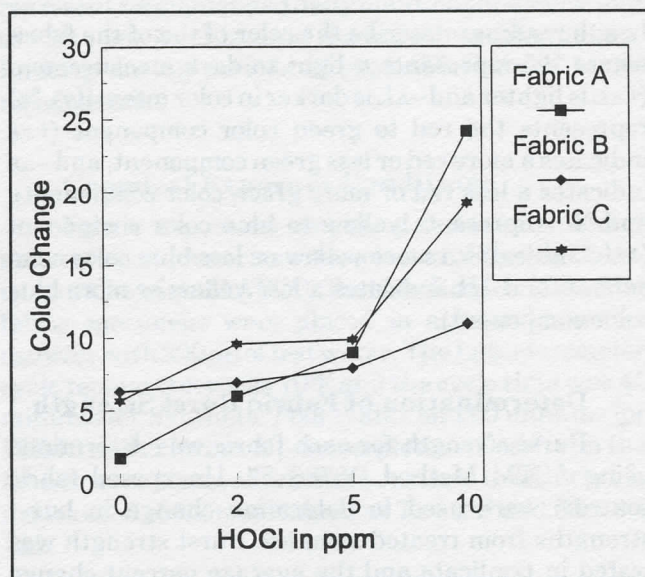
The addition of light exposure to chemical exposure greatly increased the color loss for the previously stable fabrics B and C independent of the chemical exposure (Figure 4). With fabric B the  $\Delta E$  for all



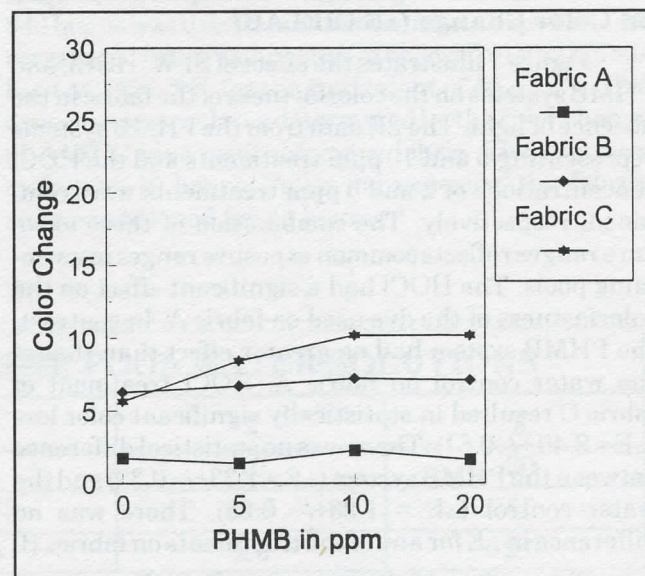
**Figure 4. Effect of Synthetic Pool Water,  $HOCl$ , and PHMB system on color change ( $\Delta E$ ) for three fabrics in the presence of light. QUV alone samples were exposed to light as dry swatches. Average  $\Delta E$  data from the  $HOCl$  2 and 5 ppm treatments and the PHMB system 5 and 10 ppm treatments were combined, respectively.**

treatments were statistically identical. With fabric C the  $\Delta E$  for QUV alone,  $HOCl$  and the PHMB system were statistically identical. For these two fabrics, the increased color loss was due to the light itself, not the sanitizer system. The pattern seen with fabric A was identical regardless of light exposure.  $HOCl$  exposure resulted in significant color loss in fabric A; whereas, the PHMB system caused no greater color loss than that of the control.

The relationship between sanitizer exposure level plus QUV on individual fabric color loss is shown in Figures 5 and 6. A strong correlation between increas-



**Figure 5. Effect of increasing concentrations of  $HOCl$  on the color change ( $\Delta E$ ) for three fabrics in the presence of light.**



**Figure 6. Effect of increasing concentrations of the PHMB system on the color change ( $\Delta E$ ) for three fabrics in the presence of light.**

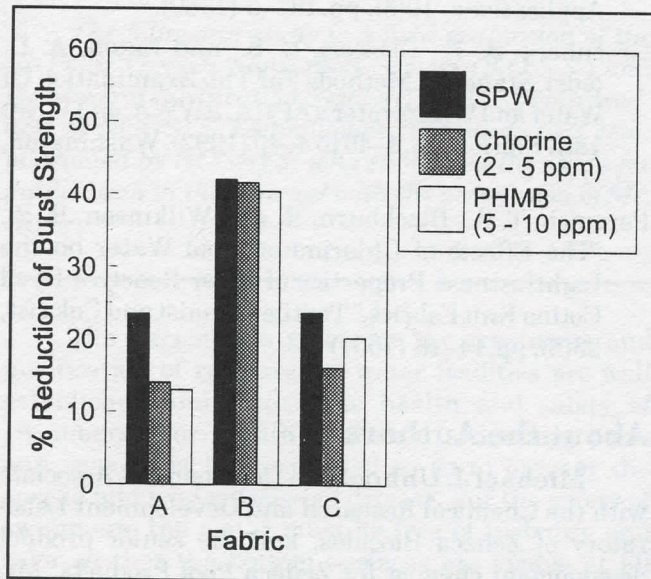
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ing concentration of HOCl versus color change in fabrics A and C was observed. The R-squared values for the corresponding curves were 0.964 and 0.927, respectively. There was no correlation observed for increasing concentration of PHMB system and color change.

### The Effect of Chemical and QUV Exposure on Burst Strength

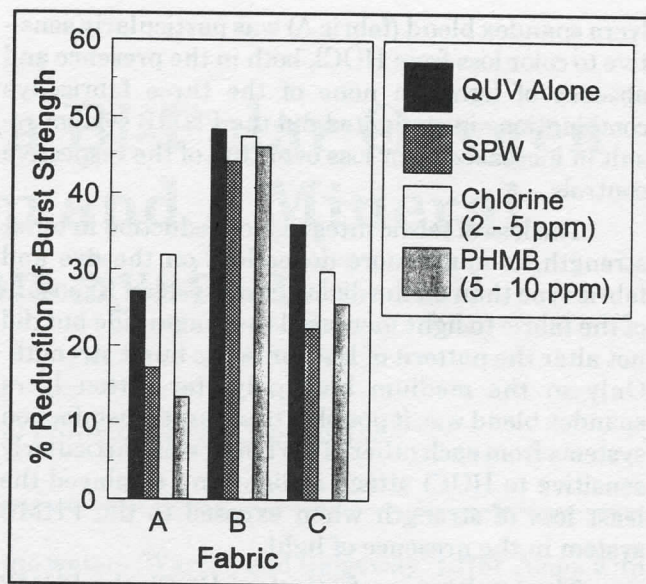
Figure 7 illustrates the effect of the SPW treatments in the absence of light on the reduction in burst strength. The most sensitive fabric to loss of burst strength was the nylon-lycra spandex blend (fabric B) which decreased in burst strength by a minimum of 40%.



**Figure 7 – Effect of Synthetic Pool Water, HOCl, and PHMB system in the absence of light on the reduction of burst strength for three fabrics. QUV alone samples were exposed to light as dry swatches. Average percent reduction data from the HOCl 2 and 5 ppm treatments and the PHMB system 5 and 10 ppm treatments were combined, respectively.**

The polyester-cotton-lycra blend (fabric A) and the all nylon (fabric C) lost an average of 16.9% and 20.1% burst strength, respectively. For all three fabrics, individual exposures were statistically indistinguishable. No trends were observed for increasing concentrations versus change in burst strength for either HOCl or PHMB system exposure and statistical relationship between dose and loss of strength could not be calculated.

Figure 8 illustrates the effect of the pool water treatments plus QUV on the reduction in burst strength. The nylon-lycra spandex blend (fabric B) was again effected the most by the chemical and QUV



**Figure 8 – Effect of Synthetic Pool Water, HOCl, and PHMB system in the presence of light on the reduction of burst strength for three fabrics. QUV alone samples were exposed to light as dry swatches. Average percent reduction data from the HOCl 2 and 5 ppm treatments and the PHMB system 5 and 10 ppm treatments were combined, respectively.**

exposure with an average of treatments resulting in a 46.6% loss of burst strength. All four treatments for fabric B were statistically identical. Average strength loss for fabric C was 28.5%. The QUV treatment alone resulted in a 36.1% strength loss which was significantly different than the other treatments. HOCl, PHMB system, and the SPW control were statistically identical. The polyester-cotton-lycra blend (fabric A) was the least affected and lost an average of 22.4% strength. The reduction in burst strength from HOCl exposure was statistically greater (32.0%  $\pm$  1.9) than that from QUV alone (27.2%  $\pm$  2.2) or the PHMB system (13.4%  $\pm$  1.9). The SPW treatment loss was 17.2%  $\pm$  14.3. The high standard error of the SPW treatment remains unexplained.

### SUMMARY AND CONCLUSIONS

The most controllable factor in degradation of swimwear, and perhaps the most notable to the observer, is the color loss pattern. The dye and fabric type used are significant factors in determining the colorfastness. The pink 100% nylon fabric (fabric C) was the most resistant to color change from disinfectants in the absence of artificial light. The chartreuse nylon-lycra spandex blend (fabric B) was slightly less colorfast to HOCl in the absence of light. Both fabrics showed increased color loss during exposure to artificial sunlight regardless of which disinfection system was employed. The medium blue polyester-cotton-



lycra spandex blend (fabric A) was particularly sensitive to color loss from HOCl, both in the presence and absence of light. In none of the three fabric-dye combinations investigated did the PHMB system result in increased color loss over that of the respective controls.

The loss of fabric integrity, or reduction in burst strength, is much more dependent on the dye and fabric type than on the disinfection system. Exposure of the fabric to light increased the magnitude but did not alter the pattern of loss for fabric burst strength. Only in the medium blue polyester-cotton-lycra spandex blend was it possible to separate disinfection systems from each other. This fabric was particularly sensitive to HOCl attack in light and displayed the least loss of strength when exposed to the PHMB system in the presence of light.

The mechanism of attack of HOCl, the PHMB system and sunlight on fabric are quite different and displayed differential effects on fabric properties. HOCl is a commonly employed bleaching agent with a high electromotive potential. The PHMB system used in recreational water consists of PHMB, hydrogen peroxide, and a QAC. It is unlikely that the PHMB or the QAC in the system contribute to color change or the reduction in burst strength. Effects observed with the PHMB system are probably attributable to the hydrogen peroxide. Sunlight results in color loss and fabric disintegration as a result of UV degradation.

The observed pattern of increased color loss and fabric degradation after exposure to artificial sunlight raises serious concerns about the proper method of drying swimwear. The common practice is either to dry the swimsuit while wearing it in the sun, or remove it and dry the suit in direct sunlight. During normal use the suits are exposed to pool water treatment chemicals that will have had some detrimental effect on the color and integrity of the swimwear. This effect will be greatly increased by the exposure to sunlight. The results of this study suggest that to extend swimwear life it should be allowed to dry by means other than using direct sunlight. Improved color stability for colorfast swimwear can be achieved by encouraging bathers to dry wet suits in indirect light. The drying of inherently non-colorfast swimwear in indirect sun light is not likely to reduce color loss after exposure to HOCl.

## Acknowledgment

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