

# The Effects of Chlorinated Water on Polyethylene Pipes

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## ABSTRACT

**Chlorine chemistry is complex. Under certain common conditions, chlorinated compounds can react with polyethylene pipes causing premature failures (bursts/leaks). It is important to understand this degradation mechanism in order to prevent future premature pipe failure. Recently, a specific additive system, when incorporated into polyethylene pipe resin was demonstrated to significantly improve the pipe's resistance to degradation caused by chlorine exposure.**

## BACKGROUND

Disinfected drinking water is critical for maintaining the healthy and sanitary conditions we enjoy today. Before 1915, unsafe drinking water caused a significant number of deaths due to cholera, dysentery, hepatitis A and typhoid fever. Abel Wolman, as the Chief Engineer of the Maryland State Department of Health from 1922-1939<sup>(1)</sup>, made the important contribution of chlorinating the Baltimore drinking water supply. The cities of New York, Detroit and Columbus (OH) quickly followed in chlorinating their drinking water supplies. By the late 1920's, this practice was widely accepted nationwide and an 85% drop in typhoid fever death was reported.

Drinking water chlorination also offers additional benefits of<sup>(2)</sup>:

- Reducing many disagreeable tastes and odor
- Eliminating slime bacteria, molds and algae
- Reducing hydrogen sulfide, ammonia and other nitrogen compounds
- Removing iron and manganese in water

Since 1974, the US Environmental Protection Agency (EPA) was given authority to set water quality standards. Even though EPA requires a minimum level of disinfectants in the water, maximums are set as follows: 4mg/l for elemental chlorine and 4mg/l for chloramine.

Starting in the 1940's, thermoplastic pipe began to be used to transport drinking water. Since its introduction and further coupled with technical advancement, plastic pipe applications have greatly expanded. Today, plastic pipe offers improved long-term performance, corrosion resistance, scaling resistance, abrasion resistance, physical property flexibility, cost efficiency (lower labor cost – ease of installation), coilability, low coefficient of friction and lightweighting compared to metal pipes. These advantages allowed thermoplastic pipes to replace metal and brick water distribution technology.

Today plastic pipes are used in communication cable protection, hot water heating, waste water transport, potable water distribution and irrigation.

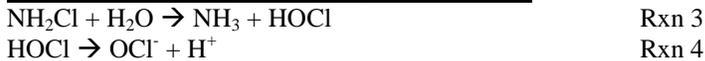
## DISCUSSION

While thermoplastic pipe has good corrosion resistance, it unfortunately is not impervious to attack by chlorine-based disinfectants. The most common disinfectants for drinking water are chlorine gas, chloramines and sodium hypochlorite/calcium hypochlorite. They all work by generating “free chlorine” (HOCl and OCl<sup>-</sup>). With the expanding application of plastic pipes and the use of chlorinated water, the physical properties of polyethylene pipe are under severe degradation stress. Below illustrates the formation of the disinfectant free chlorine (HOCl and OCl<sup>-</sup>) from chlorine gas, chloramines and metal hypochlorite.

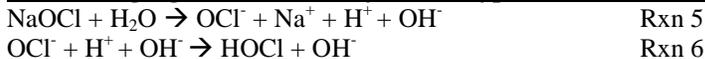
### Disinfecting Agent Formation by Chlorine



### Disinfecting Agent Formation by Chloramines



### Disinfecting Agent Formation by Metal Hypochlorite (NaOCl/CaOCl)



Hypochlorous acid (HOCl) is considered an oxidizer (the active sanitizing agent) that can neutralize harmful germs, bacteria and pathogens as well as react with polyethylene pipe. The concentration of HOCl is highly dependent on pH. At a pH of 5.5, HOCl is estimated to be undissociated while at pH of 11 HOCl is completely dissociated. Also at a pH of less than one, Cl<sub>2</sub> gas formation can be expected.

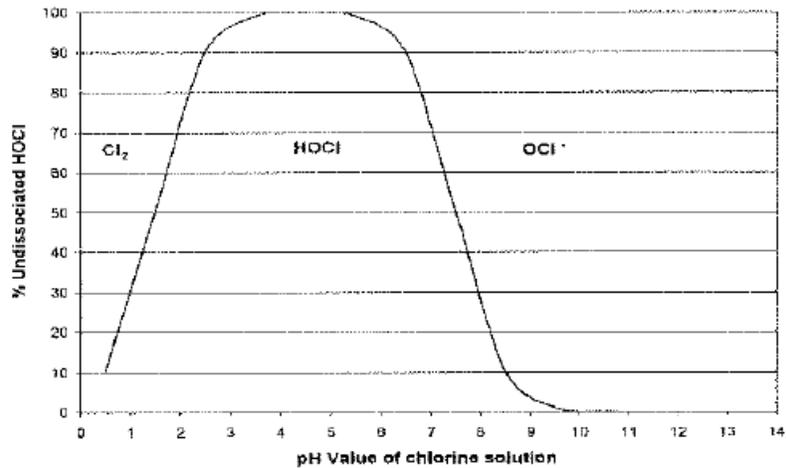
The following illustrates the reaction pathway for the dissociation and undissociated HOCl which is dependent on pH<sup>(3)</sup> (see Figure 1).



The recommended pH for safe and effective sanitizing is between the ranges of 6.5 to 7.5.

It has been documented<sup>(4)</sup> that polyethylene pipes undergo degradation, but little has been written to explain how this polymer can be degraded by hypochlorous acid in an environment that is heterogeneous (solid phase and aqueous phase), free of harmful UV energy and at relatively low temperatures. The degradation mechanism may seem difficult to explain given the relatively mild conditions of commercial use. The concepts below may shed some light on the potential degradation pathway.

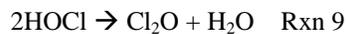
Figure 1 -- Effect of pH on hypochlorous acid content.



One study<sup>(5)</sup> has shown that hypochlorous acid can react with iron(II) complex ( $\text{Fe}^{+2}$ ) in aqueous solution with the rate constant  $220 \pm 15 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . In this reaction, free hydroxyl radicals are formed in 27% yield. The hydroxyl radical and chlorine radical can then initiate the degradation of polyethylene pipe.



Another study<sup>(6)</sup> showed that saturated alkanes can be oxidized by hypochlorous acid in darkness, in a two-phase system, and at relatively low temperatures ( $0\text{-}50^\circ\text{C}$ ). This study implicated  $\text{Cl}_2\text{O}$ , generated from hypochlorous acid according to Rxn 9, as the radical generating species.



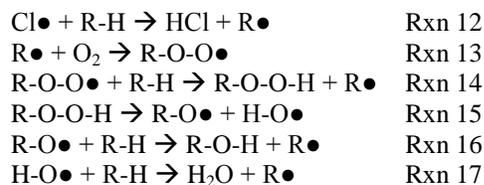
The authors of this study proposed two possible mechanisms for the initiation of free-radical chains. The first involves cleavage of the Cl-O bond in the  $\text{Cl}_2\text{O}$ , which they claim is possible due to the high electronegativity of the Cl and O.



Another potential pathway for the free radical initiation is an electron transfer process between the polyethylene pipe and the chlorinating compound ( $\text{Cl}_2\text{O}$ ). The scientists drew an analogy between this reaction and the spontaneous free radical fluorination of hydrocarbons by elemental fluorine<sup>(7)</sup>.



The generation of R• and Cl• in Rxn 10 and Rxn 11 can lead to the accelerated degradation of the polyethylene pipe. The polyethylene degradation pathway is described below (Rxn 12 to Rxn 17).



## EXPERIMENTAL

In the first phase of this study, commercial polyethylene pipes were obtained and immersed in deionized (DI) water while another set was immersed in chlorine water. The concentration of chlorine in the chlorinated DI water was fixed at 5ppm of free chlorine using calcium hypochlorite, at an initial pH of approximately 6.8. This study was carried out at 60°C for both the DI and Cl water. General Signal Blue M forced air convection ovens were used as the heating apparatus. The DI water and Cl water solutions were refreshed once a week. At one week intervals, the OIT and carbonyl growth (via FTIR w/ ATR) were measured and recorded. Oxidative induction times (OIT) were measured following ASTM Designation D3895-98<sup>(8)</sup>. The surface of the pipe samples were sliced using a diamond tipped microknife blade. The infrared spectra of the sliced pipe samples were acquired using a single reflection diamond ATR accessory attached to a Digilab UMA 600 infrared microscope. The microscope was coupled to the Digilab 7000e FTIR spectrophotometer. The carbonyl band is located at 1715 cm<sup>-1</sup>.

SEM analysis was performed using a Zeiss DSM 982 FEG-SEM equipped with a PGT EDX detector. Spectra were collected at 20 KeV providing magnification as high as 5000x magnification.

In the second phase of the study, several developmental compounds were evaluated to measure their effect on increasing the polyethylene pipe resistance to degradation caused by exposure to the strongly oxidizing free chlorine.

In this part of the study, pipes were modeled with commercial grade polyethylene resin. Additive packages were compound extruded on a Davis Standard extruder with a one inch single mixing screw. The extrusion temperature was set between 175-195°C. Upon exiting the water bath, the extrudate was pelletized and collected. The pellets were injection molded into 120 mils plaques. The Arburg, Inc.'s Allrounder injection molding machine (190-210°C) was used to produce the tensile bars and plaques.

The plaques were also immersed in glass containers containing DI water or 5 ppm chlorinated water (weekly refreshed). Also on a weekly basis, the OIT, yellowness index and total color change were measured and recorded.

## RESULTS

### *Phase 1: Commercial Pipe Evaluation*

The effects of hypochlorous acid on commercial grade polyethylene pipe were measured using standard ASTM OIT methods after exposure in a 60°C aqueous solution of 5ppm of free chlorine using calcium hypochlorite (7.3ppms of calcium hypochlorite). In parallel, samples were soaked in 60°C deionized water to create a comparative baseline to measure the extent of polymer degradation. At seven day intervals the calcium hypochlorite solution and water were renewed and the samples re-soaked.

Initial OIT of the commercial pipe was determined to be 145 minutes. After immersion for 5 weeks in 60°C water, OIT's of 124 minutes were measured and recorded. However in the sample immersed in 5ppms free chlorine, after 5 weeks at 60°C, the OIT significantly decreased to 49 minutes. Below, Table 1 and Figure 1 show the affects of free chlorine and water on commercial pipe samples.

**Table 1: OIT of pipe samples immersed in water and 5ppm free chlorine**

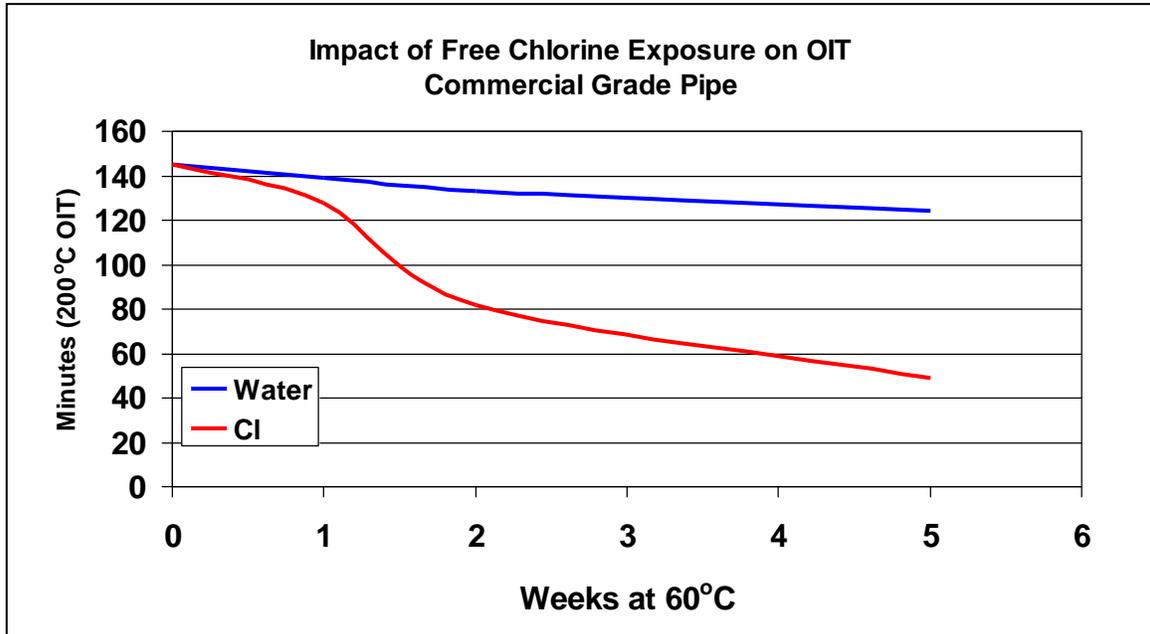
|                           | MINUTES (OIT at 200°C) |
|---------------------------|------------------------|
| Unexposed Commercial Pipe | 145                    |

|                           | MINUTES (OIT at 200°C) |
|---------------------------|------------------------|
| Unexposed Commercial Pipe | 145                    |
| 2 weeks at 60°C in water  | 133                    |
| 5 weeks at 60°C in water  | 124                    |

|                           | MINUTES (OIT at 200°C) |
|---------------------------|------------------------|
| Unexposed Commercial Pipe | 145                    |
| 1 weeks at 60°C in Cl     | 128                    |
| 2 weeks at 60°C in Cl     | 82                     |
| 5 weeks at 60°C in Cl     | 49                     |

The OIT results indicated in 60°C water, the polyethylene pipe oxygen induction time decreases slightly over time. However, with just 5ppms of free chlorine, oxygen induction time decreases significantly more quickly. After 5 weeks in water, the OIT was measured and recorded at 86% of its original value while in 5ppm free chlorine water; the OIT was measured at only 34% of its original value.

**Figure 1: OIT of pipe samples immersed in water and 5ppm free chlorine**



The degradative oxidation of polyethylene can lead to the formation of the carbonyl chemical functionality. A technique to determine the extent of degradation/oxidation of polyethylene is to evaluate and measure the carbonyl functionality on the pipe's surface.

FTIR/ATR is a method developed to measure the carbonyl chemical functionality ( $1715\text{ cm}^{-1}$ ) at the pipe's surface in order to understand the extent of surface oxidation. Below Figures 2 and 3 shows the results of carbonyl formation of the pipe in water and free chlorine immersion.

Figure 2: Infrared reflection spectra of HDPE after 3 weeks in 60°C water with and without 5 ppm chlorine.

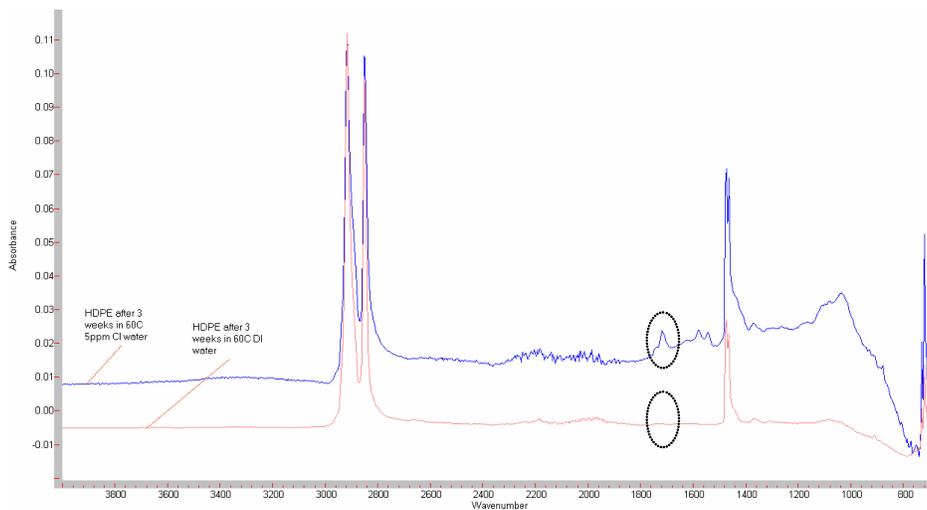
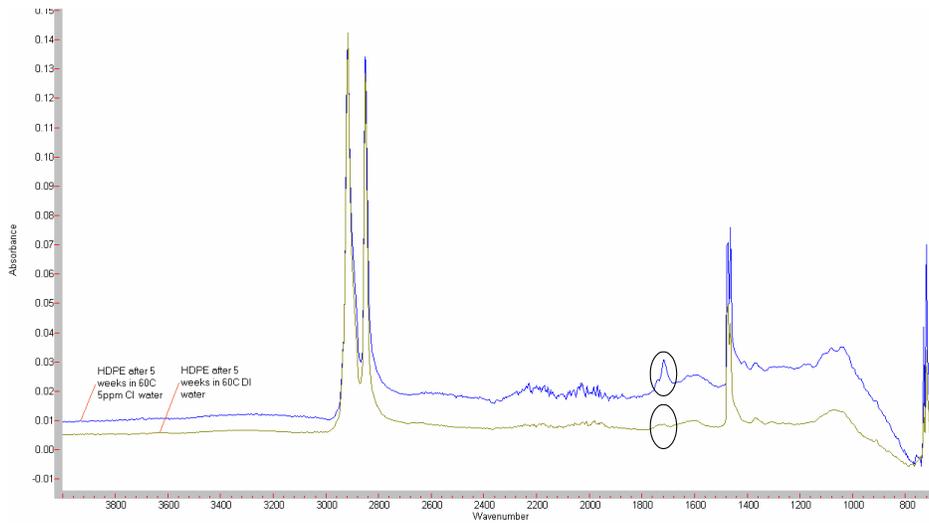


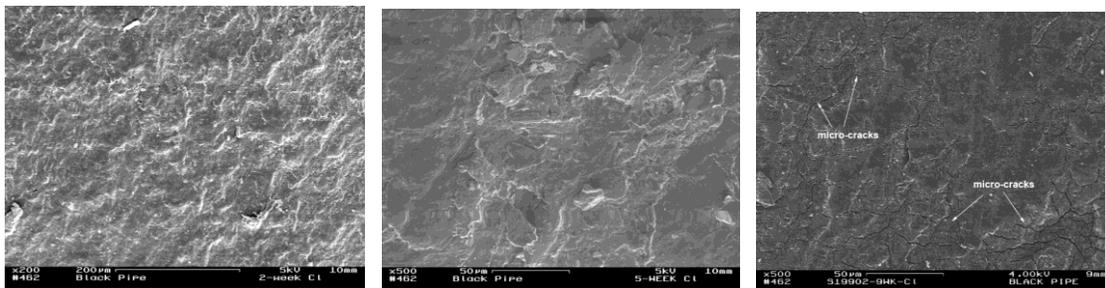
Figure 3: Infrared reflection spectra of HDPE after 5 weeks in 60°C water with and without 5 ppm chlorine.



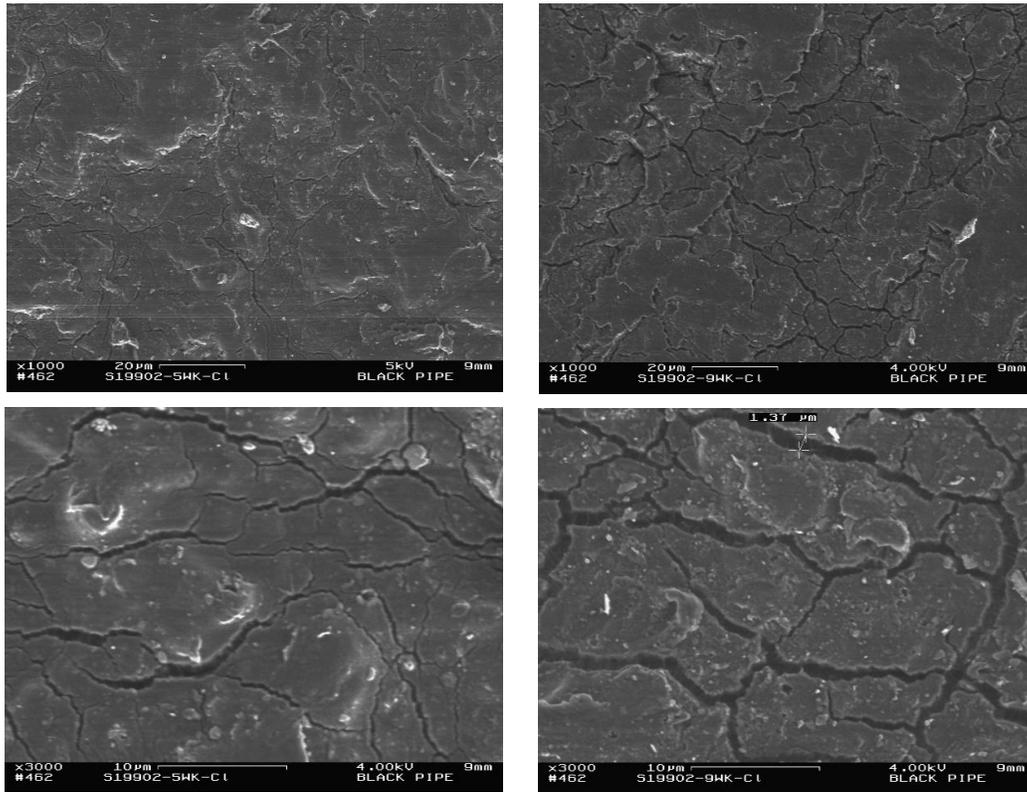
At the 3<sup>rd</sup> and 5<sup>th</sup> week of immersion at 60°C water, the commercial pipe sample showed no appreciable surface formation of the carbonyl functionality. At 1715 cm<sup>-1</sup> wavelength, the formation of the absorption peak associated with carbonyl groups is insignificant. On the other hand after 3 and 5 weeks of immersion at 60°C water containing 5ppm of free chlorine, a well defined carbonyl peak at 1715 cm<sup>-1</sup> was observed at the surface of the commercial pipe. This peak can be attributed to the accelerated oxidative degradation at the surface of the commercial polyethylene pipe.

Another analytical method employed to evaluate the extent of degradation in pipe is scanning electron microscopy (SEM). SEM offers a hyper-magnification visual inspection of the surface, and can allow observation of the surface imperfections, such as micro-cracks. Micro-cracks less than 1 um can be visually observed. Below, Figures 4 and 5 pictorially illustrate the visual surface inspection via SEM techniques.

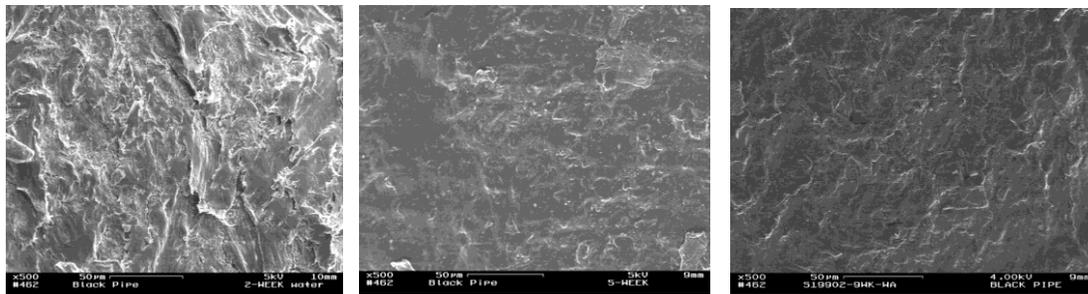
**Figure 4: Commercial Pipe Immersed in Free Chlorine (HOCL and OCl<sup>-</sup>)  
Low Magnification: Macro crack not observed via SEM Analysis (200x and 500x)**



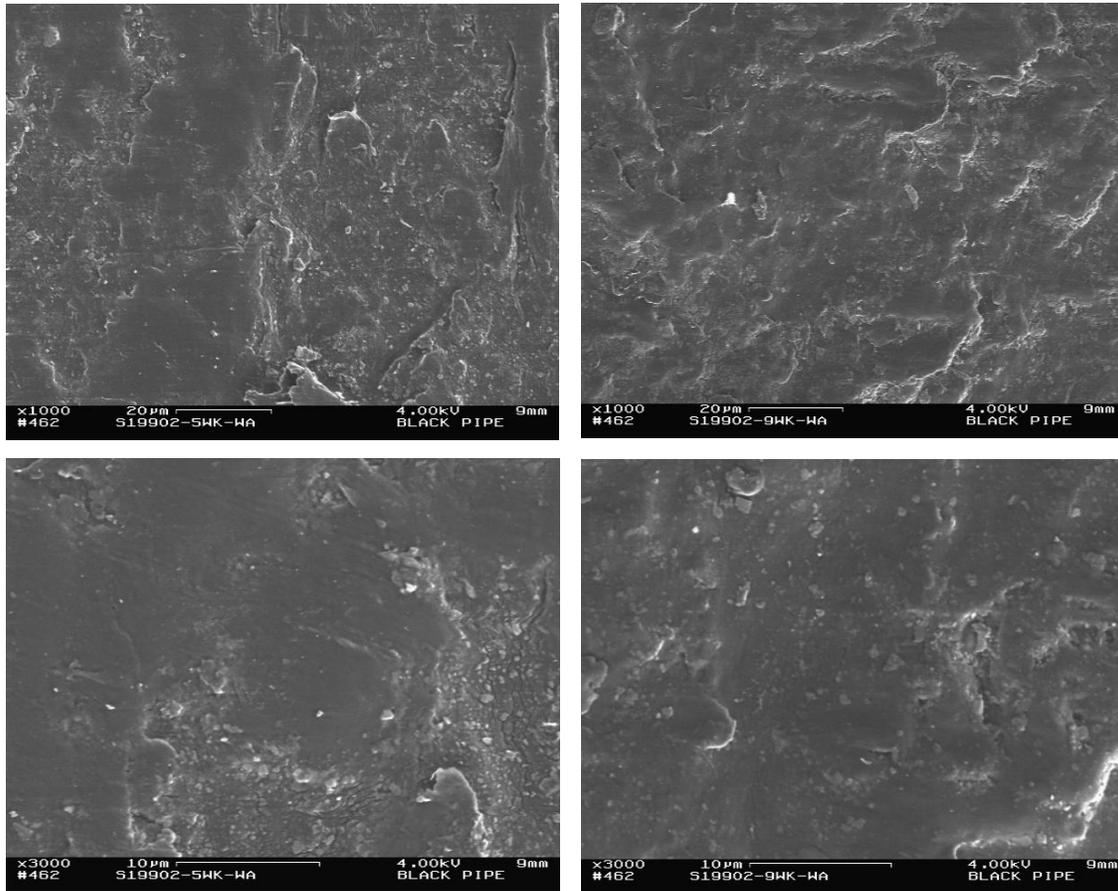
**High Magnification: Onset of micro cracks observed via SEM Analysis (1000x and 3000x)**



**Figure 5: Commercial Pipe Immersed in DI Water  
Low Magnification: 2, 5 and 9 weeks (500x)**



### High Magnification: 5 and 9 weeks (1000x and 3000x)



Visual microscopic inspection via SEM indicated the commercial pipe immersed in water for 2, 5 and 9 weeks showed no microcracks at 500x, 1000x and 3000x magnification. See Figure 5. However at magnification of 1000x and 3000x, microcracks between 0.5-1.3 μm were observed in pipe samples immersed in 5ppms free chlorine water for 5 weeks and larger cracks appeared after 9 weeks of immersion. See Figure 4.

#### Phase 2: Chlorine Resistance of Polyethylene with New Specialty Additives

After defining the deleterious affects of free chlorine water to polyethylene pipes, three proprietary specialty additives were evaluated to counter the degradation effects of free chlorine on polyethylene.

The first test included the OIT measurements on control and stabilized samples. The proprietary specialty additives are identified as Compound A, B and C in the following table.

**Table 2: Initial OIT of polyethylene samples**

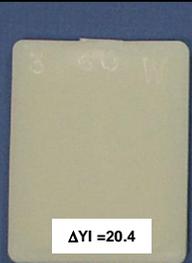
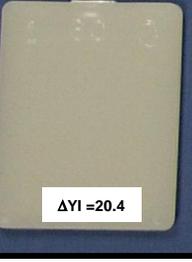
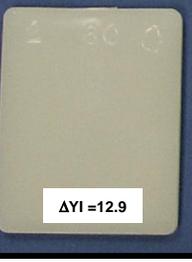
|                          | MINUTES (OIT at 200°C) |
|--------------------------|------------------------|
| Unexposed Control Sample | 104                    |

**Table 3: OIT of polyethylene samples immersed in water with 5ppm free chlorine 3 Weeks at 85°C, 5ppm free chlorine**

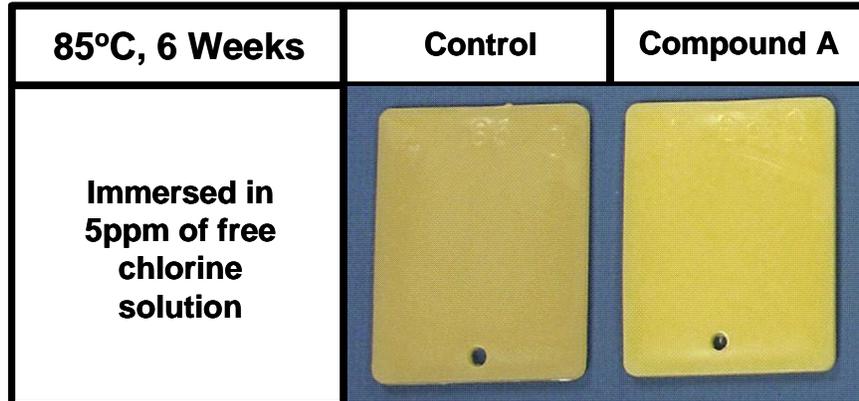
|                     | MINUTES (OIT at 200°C) |
|---------------------|------------------------|
| Control Sample      | 42                     |
| Additive Compound A | 100                    |
| Additive Compound B | 37                     |
| Additive Compound C | 15                     |

The OIT of the unexposed sample started with a time of 104 minutes. After 3 weeks in 5ppm free chlorine water at 85°C, the sample OIT dropped to 42 minutes (-60% decrease from original value). However with the incorporation of a specialty additive, Compound A, the OIT was measured and recorded at 100 minutes (less than 4% decrease from original value). New Compounds B and C did not show a positive effect.

Color stability can be important in certain applications. Pictures of the plaques can be seen below. It was generally noted that with prolonged exposure to free chlorine, sample yellowed and then darkened.

| 60°C, 6 Weeks                              | Control   | Compound A  | Compound B   | Compound C  |
|--|---|---|--|---|
| Immersed in DI Water                       | <br>$\Delta YI = 17.9$ | <br>$\Delta YI = 9.9$  | <br>$\Delta YI = 20.4$ | <br>$\Delta YI = 13.4$ |
| Immersed in 5ppm of free chlorine solution | <br>$\Delta YI = 20.4$ | <br>$\Delta YI = 12.9$ | <br>$\Delta YI = 24.6$ | <br>$\Delta YI = 29.3$ |

After being immersed for 6 weeks in 5ppm free chlorine water at 60°C, the control plaque increased 20.4 units in yellowness index (YI) while the Compound A plaque increased only 12.9 YI units.



### CONCLUSION

In this study, the degradation of commercial grade polyethylene pipe can accelerate under exposure to free chlorine. Accelerated degradation was observed with a significant decrease in OIT versus samples which did not contain free chlorine. Early carbonyl formation was observed at the surface of the free chlorine exposed pipe when compared to a sample exposed to “water only”. Premature formation of micro cracks was observed at the surface of the free chlorine exposed pipe.

Several additive compounds were evaluated in order to increase the pipe’s resistance to free chlorine oxidative degradation. Compound A was found to maintain the pipe’s original OIT even under exposure to 5ppms of free chlorine after 3 weeks at 85°C. Further studies are planned to optimize and enhance the performance of polyethylene pipe under free chlorine exposure.

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