

## Introduction

Using corrosion inhibitors in polyethylene glycol (PEG) solutions for the treatment of non-separable metal/wood composite artifacts recovered from the marine environment has been well studied (Cook *et al.*, 1985; Gilberg *et al.*, 1989; Selwyn *et al.*, 1993). Of these inhibitors, Hostacor IT® is the most well documented for the treatment of such composite objects (Argyropoulos *et al.*, 1999; Guilminot, 2000; Memet and Tran, 2005). Unfortunately it is no longer being produced. Studies have been ongoing at The Mariners' Museum and Park (TMMP) in Newport News, Virginia, USA on the use of sodium nitrite ( $\text{NaNO}_2$ ) as a replacement corrosion inhibitor for Hostacor IT®.  $\text{NaNO}_2$  presents several advantages including a near neutral pH, is effective at a low concentration, applicable to several metals, and has a theoretical compatibility with organic materials. It was demonstrated that  $\text{NaNO}_2$  can be used as an option in storage solutions for marine iron alloys and, after desalination, to prevent flash corrosion during rinsing baths (Sangouard *et al.* 2015; Hoffman, *unpublished*). Recent results also showed that 1000 parts-per-million (ppm)  $\text{NaNO}_2$  prevents iron corrosion in 20%v/v PEG 400 solutions absent of chlorides (Sullivan *et al.* 2016). Despite these promising results, before fully supporting the use of  $\text{NaNO}_2$  for the treatment of non-separable iron/wood composite objects, further research was required to identify that  $\text{NaNO}_2$  has no negative impact on the wood structure and its long-term stability after treatment.

## Method

Waterlogged red oak samples were cut into 2.5 cm squares and placed in solutions of 20% v/v PEG 400, 40% w/v PEG 2000 and a mixture of 10% v/v PEG 400 and 30% w/v PEG 4000 with and without the addition of 1000ppm  $\text{NaNO}_2$ . Four samples were placed in each solution. Following impregnation, the wood samples were freeze-dried using a VirTis 24 x 48 general purpose freeze-dryer. The chamber was set to  $-22^\circ\text{C}$  and the condenser  $-52^\circ\text{C}$  with a vacuum of 15 mtorr. Samples were then evaluated visually and with colorimetry to determine if treatment solution impacted final appearance. Colorimetry measurements were taken using a C-241 Minolta colorimeter after treatment. Environmental scanning electron microscope (SEM) images of the samples were taken with a Phenom ProX Desktop SEM to assess any possible change in the cellular structure of the wood. Samples of the solutions were also freeze-dried to reduce water content and then analyzed with FTIR. This will show if  $\text{NaNO}_2$  impacts the molecular structure of PEG or causes organic compounds to be extracted from the wood. A Thermo-Nicolet Nexus 670 FTIR was employed for analyses of the solutions before and after treatment.

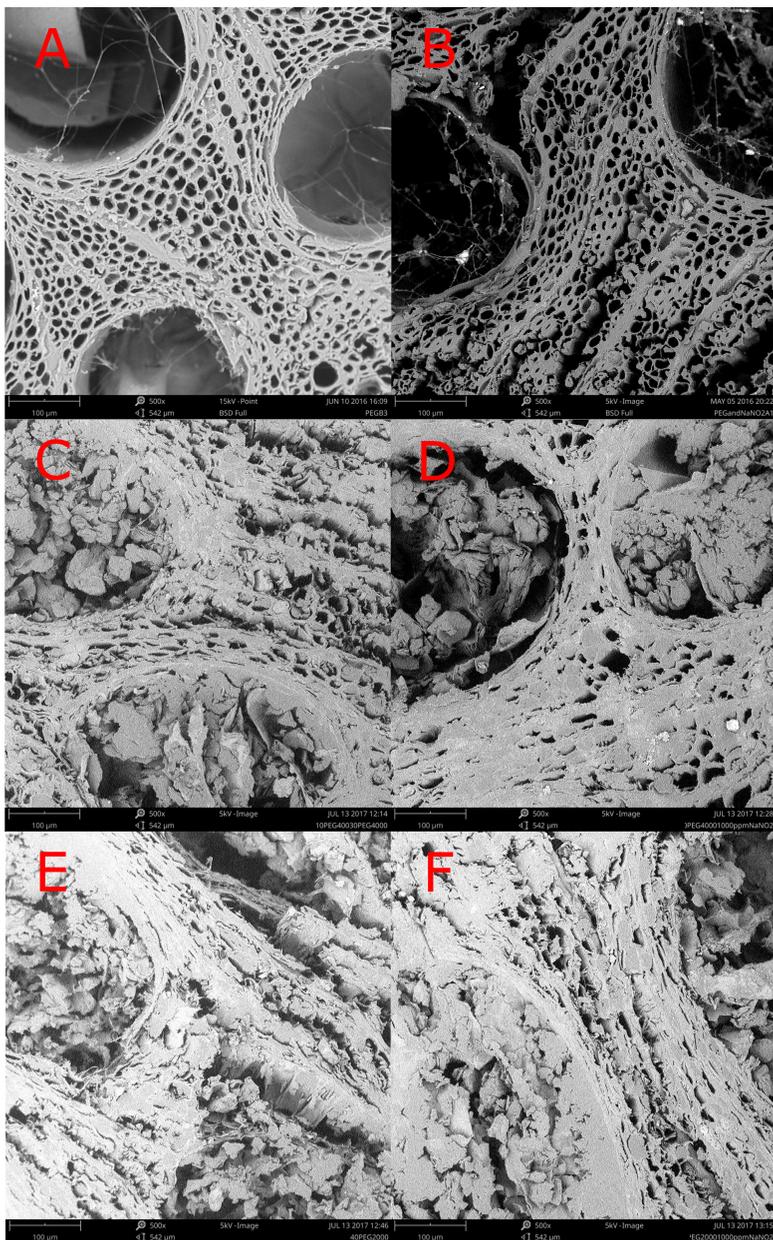


Figure 3: SEM images of wood samples after experimentation A: 20% PEG 400 in deionized water. B: 20% PEG 400 in 1000ppm  $\text{NaNO}_2$  in deionized water. C: 10% PEG 400 + 30% PEG 4000 in deionized water. D: 10% PEG 400 + 30% PEG 4000 in 1000ppm  $\text{NaNO}_2$  in deionized water. E: 40% PEG 2000 in deionized water. F: 40% PEG 2000 in 1000ppm  $\text{NaNO}_2$  in deionized water.

## Discussion and Conclusion

In light of these results  $\text{NaNO}_2$  does not seem to impact wood negatively or otherwise. While long term testing should be undertaken, it seems that  $\text{NaNO}_2$  is a viable option as a corrosion inhibitor for conservators treating waterlogged artifacts composed of wood and iron in PEG solutions. It is important to note that it is best to desalinate an object before using  $\text{NaNO}_2$  as chlorides will compete at the surface of the metal with the corrosion inhibitor impacting its efficiency. Sodium nitrite is currently being used at TMMP as a corrosion inhibitor for the treatment of non-separable composite artifacts composed of waterlogged wood and wrought iron. Testing is also ongoing for the use of  $\text{NaNO}_2$  with copper alloys in PEG.



Figure 1: Wooden samples treated with 10% PEG 400 + 30% PEG 4000 with and without  $\text{NaNO}_2$ , and 40% PEG 2000 with and without  $\text{NaNO}_2$ .

	L	a	b	$\Delta E^*_{ab}$
Control samples (freeze-dried without treatment)	36.77	4.93	14.76	-
20% PEG 400	43.21	5.34	17.56	7.20
20% PEG 400 + 1000ppm $\text{NaNO}_2$	38.04	4.54	15.79	4.92
10% PEG 400 + 30% PEG 4000	38.51	5.15	15.10	4.74
10% PEG 400 + 30% PEG 4000 + 1000ppm $\text{NaNO}_2$	34.65	4.43	11.77	4.35
40% PEG 2000	36.41	5.92	15.22	4.96
40% PEG 2000 + 1000ppm $\text{NaNO}_2$	33.51	5.80	12.75	4.90

Table 1: CIELAB colorimetry measurements: each wooden sample's color was measured, after treatment, and the colors data were averaged. The  $\Delta E^*_{ab}$  was calculated against the control samples.

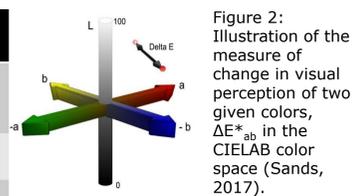


Figure 2: Illustration of the measure of change in visual perception of two given colors,  $\Delta E^*_{ab}$  in the CIELAB color space (Sands, 2017).

Delta E	Perception
$\leq 1.0$	Not perceptible by human eyes.
1 - 2	Perceptible through close observation.
2 - 10	Perceptible at a glance.
11 - 49	Colors are more similar than opposite
100	Colors are exact opposite

Table 2:  $\Delta E^*_{ab}$  perception scale (Schuessler, 2017).

## Results

Visually, the only samples noticeably different are those that were treated with PEG 400 without the addition of  $\text{NaNO}_2$ . They appear slightly lighter than the others. The remaining samples, even those that received no treatment have barely any detectable difference in color (Fig. 1).

Colorimetry measurements confirmed these observations and show that the change in color between treated samples and untreated samples is only noticeable at a glance ( $\Delta E^*_{ab}$  max. is 7.20, Table 1-2, Fig.2). These measurements also confirm that, whether  $\text{NaNO}_2$  was used or not, change in color is not perceptible by the human eyes amongst treated samples ( $\Delta E^*_{ab}$  varies from 4.3 to 4.9, i.e. less than 1  $\Delta E^*_{ab}$  unit). Samples treated with PEG 400 without  $\text{NaNO}_2$  vary visually, at a glance (3  $\Delta E^*_{ab}$  units compared to the rest of the treated samples), confirming visual observations of these samples being lighter.

SEM images show no  $\text{NaNO}_2$  residue on the wood cells. There is no observable difference in the cellular structure of samples treated with and without the addition of  $\text{NaNO}_2$  (Fig. 3)

The FTIR spectrum demonstrate that the addition of  $\text{NaNO}_2$  is not changing the structure of the PEG in solution and is not extracting anything detectable by FTIR from the wood (Fig. 4).

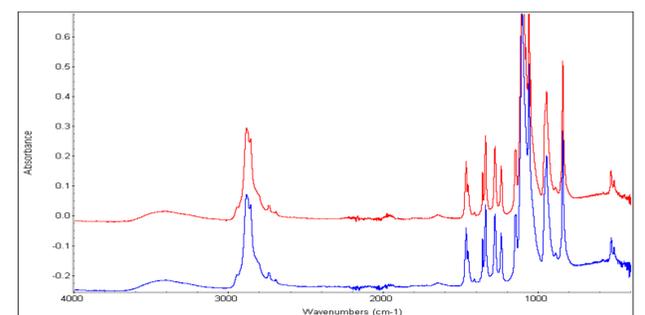


Figure 4: FTIR spectra of 40% w/v PEG 2000 in deionized water (red) versus 40% w/v PEG 2000 + 1000ppm  $\text{NaNO}_2$  in deionized water (blue), after treatment of the wooden samples and freeze-drying of the solutions. No difference can be observed. The same results were obtained with PEG 400, and PEG 400/4000 with and without  $\text{NaNO}_2$ .

## Credits, Acknowledgements, and References

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- Argyropoulos, V. *et al.* 1999. Testing Hostacor IT as a corrosion inhibitor for iron in polyethylene glycol solutions. *Studies in Conservation*, 44(1): 49-57.
- Cook, C. *et al.* 1984. Experiments with aqueous treatments for waterlogged wood-metal objects. In *Waterlogged wood: study and conservation: proceeding of the 2nd ICOM Waterlogged Wood Working Group Conference*, Grenoble, 28-31 August 1984. eds. R. Ramière and M. Colardelle, p.147-159. Grenoble: ICOM-CC WOAM.
- Gilberg, M. *et al.* 1987. Treatment of iron/wood composite materials. In *Conservation of wet wood and metal*, *Proceeding of the ICOM conservation working groups on wet organic archaeological materials and metals*, Fremantle, 1987, eds. I. MacLeod, p.265-270. Fremantle: ICOM-CC WOAM.
- Guilminot, E. 2000. Action d'un inhibiteur de corrosion du fer en milieu eau-polyéthylène glycol (PEG) 400 lors des traitements des objets archéologiques composites de bois gorgés d'eau/fer. Ph.D. dissertation, Institut National de Polytechnique de Grenoble, France.
- Hoffman, W., and R. Spohn. 2015. Internal report. USS Monitor Center at The Mariners' Museum and Park, Newport News, VA, USA.
- Memet, J., and T. Khô. Development of a conservation treatment process adapted to archaeological iron/waterlogged wood composites. In *Proceeding of the 9th ICOM Group on Wet Organic Archaeological Materials Conference*, Copenhagen, 2004, eds. P. Hoffmann, p.437-460. Bremerhaven: ICOM-WOAM.
- Sands, S. 23 February 2016. Delta E: A Key to Understanding Lightfastness Readings. <http://www.justpaint.org/wp-content/uploads/2016/02/CIE-Lab-Delta-E-Illustration.jpg> (accessed 8 August 2017).
- Sangouard, E., *et al.* 2015. Evaluation of sodium nitrite as a corrosion inhibitor for USS Monitor artifacts. *Studies in Conservation* 60(4): 253-266.
- Schuessler, Z. Delta E 101. <http://zschuessler.github.io/DeltaE/learn/> (accessed 8 August 2017).
- Selwyn, Lyndie S. *et al.* 1993. Metal corrosion rates in aqueous treatments for waterlogged wood-metal composites. *Studies in Conservation*, 38(3): 180-197.
- Sullivan, K., *et al.* 2016. Sodium nitrite as a corrosion inhibitor in polyethylene glycol solutions for the treatment of waterlogged wooden artifacts with ferrous components. Upcoming in the *Proceedings of the 13th ICOM-CC Group on Wet Organic Archaeological Materials Conference*, Florence, Italy.