Best Available Technology for Sodium Hypochlorite Storage Tanks

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ABSTRACT

Sodium hypochlorite disinfection has become the most common chemical treatment for waste water in North America. With the ever-heightening scrutiny around transportation of chlorine, manufacturers are choosing to transport concentrated bleach instead. Waste water treatment facilities and sodium hypochlorite manufacturers have a variety of construction materials from which to choose when designing storage tanks for this corrosive chemical liquid. Stainless steel is reasonable durable but far from the most economical choice. Fiber reinforced thermoset polymers (FRP) have become the industry standard for hypo storage tanks as it is quite economical and gives remarkably long service life. When the best resin and cure system are selected and the fabrication design is optimized, FRP tanks will often last for decades. This paper will demonstrate best available technology for FRP tanks in sodium hypochlorite service based upon laboratory testing and extensive field service in multiple locations.

Key Words: Sodium hypochlorite, FRP Storage tanks Epoxy vinyl ester resins

INTRODUCTION

The municipal waste water treatment facilities have switched to sodium hypochlorite as the material of choice to treat the water. Elemental chlorine is no longer used because of environmental reasons. Sodium hypochlorite is an oxidizing material that is stabilized with sodium hydroxide. This makes it very corrosive toward many materials of construction. The stability of the sodium hypochlorite can also have an affect how corrosive the solution will be. The stability of sodium hypochlorite can be affected by several factors including concentration, pH, temperature and impurities such as metals present. The standard solution used in industry now ranges from 9 – 15% available chlorine. If the sodium hypochlorite is made using hard water, it will not be as stable because of metal contaminants such as iron, calcium and other metals which will make it more aggressive toward the material of construction of the storage tanks.

Many materials of construction have been used to store sodium hypochlorite. These include linear high density polyethylene, cross linked polyethylene, fiber reinforced polymers (FRP) and titanium. The best material is titanium, but it is very expensive. Linear high density polyethylene and cross linked polyethylene will give a service of 7-11 years according to Odyssey Manufacturing Co.[1] The most common material of construction for bulk sodium hypochlorite storage is FRP using a premium epoxy vinyl ester resin. If the proper resin is used, FRP tanks can provide a long lifetime with minimum maintenance required. The type of resin used to construct the FRP tank will determine how long the tank can be used. Case histories show that these tanks can last longer than 20 years if made properly. A well-specified and properly constructed FRP tank can last 20-30 years or more with corrosion barrier inspections typically every two years with minor repairs as required. An improper design and construction will result in corrosion barrier failure and structural damage in 3-5 years requiring complete replacement of the tank.

The study conducted in this paper was to identify the best resin system and corrosion barrier construction to obtain the maximum service life for sodium hypochlorite storage tanks. The testing involved both laboratory testing as well as testing in the field.

EXPERIMENTAL PROCEDURE

Laboratory testing was carried out using ASTM C-581[2] Standard Practice for Determining Chemical Resistance of Thermoset Resins Used in Glass-Fiber Reinforced Structures Intended for Liquid Service. Glass reinforced panels were made in the laboratory with each resin that was tested. The test panels were made by wetting out the veil, then wetting out 3 layers of 450 g/m^2 chopped strand glass mat and finishing with another layer of veil. The resin was cured at room temperature overnight and then post cured for 8 hours at 94°C. The panels were then cut to the desired size and the edges coated with the same resin to seal all cut edges to prevent wicking. The sample coupons were placed in resin kettles at 50°C and at 65°C that contained 10-15% sodium hypochlorite solution. The sodium hypochlorite solution was changed out once a week to keep the available chlorine concentration above 9% at all times during the test. Samples were pulled out and evaluated at 1, 3, 6, and 12 months. The evaluation consisted of Barcol hardness retention, flexural strength retention, flexural modulus retention, and visual inspection of the coupons. Coupons were also placed in two sodium hypochlorite storage tanks that were located in Thornton, CO and Westminster, CO. These coupons were taken out of the tank and sent in for evaluation at 3, 6 and 12 months.

The laboratory testing and the testing in the two storage tanks in Colorado was done on DERAKANE®[1] 411-350 epoxy vinyl ester resin (EVER1), HETRON® 922 epoxy vinyl ester resin (EVER2), HETRON® FR992 brominated epoxy vinyl ester resin (BREVER1), DERAKANE® 510A-40 brominated epoxy vinyl ester resin (BREVER2), and DERAKANE Momentum® 470-300 novolac epoxy vinyl ester resin (NEVER). The BREVER1 resin was tested with 2 layers of synthetic polyester veil and with 1 layer of synthetic polyester veil and with 1 layer of C-glass veil. The cure systems evaluated included a cobalt naphthenate (CoNap) /Methyl ethyl ketone peroxide (MEKP) cure system and a Benzoyl peroxide (BPO)/Dimethyl aniline (DMA) cure system. The other resins were only tested with 1 layer of C-glass veil and cured with BPO/DMA. All of the test coupons were post cured for 8 hours at 94°C.

RESULTS

Test results were obtained from laboratory testing in stabilized sodium hypochlorite at 50°C and are shown in Table 1. None of the test coupons showed significant reduction in flexural properties after 12 months. The visual inspections of the test coupons did show some differences in the surface attack on the coupons. The system that showed the most attack was the NEVER resin that was cured with BPO/DMA cure system. The surface of the resin had a flat finish indicating resin attack and only 40% of the edge coating remained. These two observations indicate resin attack is occurring and this resin would not be the best resin for long service life. The BREVER1 resin that was made with 2 layers of

[1] Registered Trademark of Ashland Inc.

synthetic polyester veil and cured with CoNap/MEKP curing system 0.15 parts of CoNap used to cure the resin also showed significant surface attack. This still had some gloss in places but after looking at the surface with a microscope one could see surface attack down to the polyester veil bundles. This also showed open channels where the polyester fibers in the veil used to be. This indicates that the synthetic polyester fibers are being attacked by the sodium hypochlorite. The coupons made out of BREVER1 resin with 1 layer synthetic polyester veil but was cured using BPO/DMA showed an improvement in surface appearance over the coupon that was cured with CoNap/MEKP cure system. This is probably because the cobalt metal can promote the decomposition of sodium hypochlorite at the surface of the laminate resulting in hypochlorous acid generation. This is more aggressive to the resins and will cause a faster attack on the corrosion barrier of the laminate. Some indication of attack on the polyester veil was also observed. BREVER1 resin and BREVER2 resin with 1 layer of C-glass veil and cured with BPO/DMA cure system both still had a semi gloss finish on its surface. This showed no attack on the resin after 12 months. The EVER1 and EVER2 resins, which had 1 layer of C-glass veil and cured with BPO/DMA each, had a flatter finish on the surface after 12 months. They showed less attack than was seen with the cobalt cured resin system but slightly more than the BREVER1 and BREVER2 resin systems. In contrast the NEVER resin system in the test gave the lowest surface hardness and also had only about 40% of its edge coating remaining after 12 months. The surface also lost its gloss and has a flat finish - all signs of resin attack on the resin surface.

These same coupons were placed in a sodium hypochlorite storage tank in Thornton, CO (Table 2) and in the City of Westminster, CO (Table 3) to see how the lab testing compared to real world testing. There was no difference in mechanical properties after 12 months. The visual examination of the coupons showed that only the NEVER resin coupon lost any surface gloss and showed signs of light resin attack. No differences could be seen in the other coupons that were evaluated in these tanks. This is probably because of the lower temperature that the coupons were exposed to. A longer test time would be needed to show difference in the other resin systems.

Additional coupon testing was done with BREVER1 resin at 65°C with 10% sodium hypochlorite. The first coupon was cured with cured with BPO/DMA with 1 layer of C-glass veil and the second was cured with BPO/DMA with 1 layer of synthetic polyester veil. The results are shown in Table 4. The coupon that had the polyester veil did very poorly after 12 months with no surface hardness and only 28% of its flexural properties remaining. The coupon that had the C-glass veil did much better in maintaining 47% of its original surface hardness and 70% of its flexural properties. This higher temperature accelerates the decomposition of the sodium hypochlorite and makes it a much more severe test. In the testing at 50°C, the synthetic polyester veil appears to be attacked by sodium hypochlorite and not work as well in this service.

The affect of cobalt has been shown in previous work by Don Kelley[3] that was presented at Corrosion 2004. Testing was done in 5.25% sodium hypochlorite for 10 months at 65°C. Three Coupons were made using EVER1 and cured using 0.1% CoNap/MEKP, 0.3% CoNap/MEKP and BPO/DMA. Figure 1 shows the graph of weight loss with time for these three systems. The weight loss was directly related to the amount of cobalt metal in the system. The BPO/DMA cured system which had no cobalt in it only lost 2% of its weight. The cobalt cured systems lost 18% for the 0.3% system and the 0.1% cobalt containing system lost about 7% of its weight. This should translate into longer life of a storage tank cured with BPO/DMA compared to one cured with CoNap/MEKP.

SUMMARY AND CONCLUSION

The testing that was done at ambient temperature in a sodium hypochlorite storage tank showed very little difference between a brominated vinyl ester resin and the standard bisphenol A epoxy vinyl ester resins. It was seen that the novolac epoxy vinyl ester resin was showing some signs of resin attack. The laboratory testing conducted at 50°C did distinguished a little more between the resins. It was seen that brominated epoxy vinyl ester resins showed less resin tank attack compared to standard bisphenol A epoxy vinyl ester. This testing also showed that there is no advantage to using synthetic polyester veil over C-glass veil. Some of the testing reported here would argue that C-glass veil is much better that synthetic polyester veil especially at elevated temperatures.

The factor that shows the most influence on the performance in sodium hypochlorite is the presence of cobalt in the corrosion liner. The cobalt does cause the resin to be attacked faster. It is recommended that cobalt curing systems not be used in the corrosion liner of sodium hypochlorite storage tanks.

Longer tests will have to be run to further distinguish between the brominated and standard epoxy vinyl ester resins at ambient temperatures. From the visual examination, it does appear that the brominated epoxy vinyl ester resins perform better than the standard epoxy vinyl ester resins. Case histories would also indicate that storage tanks and sodium hypochlorite reactors made out of brominated epoxy vinyl ester resins like BREVER1 and BREVER2 in this study will last longer than tanks made out of standard bisphenol A epoxy vinyl ester resins. Lower styrene containing bisphenol A epoxy vinyl ester resins in previous testing has shown that they do not perform as well in this service. That is why they were not included in the study.

RECOMMENDATIONS

The recommendation for storage tanks and equipment that will be exposed to sodium hypochlorite solutions that have available chlorine higher that 9% would be to use a corrosion liner that is fabricated out of a brominated epoxy vinyl ester resin like BREVER1 and BREVER2 described in this paper. The resin in the corrosion barrier should be cured using BPO/DMA cure system. No cobalt should be present in the corrosion liner of the equipment. Cobalt/MEKP cure systems can be used in the structural portion of the equipment. The corrosion liner should contain a minimum of 1 layer of C-glass veil, 2 layers would be better, backed by 5 mm of chopped strand boron free glass. The corrosion barrier is required to be post cured to obtain the longest service life out of the equipment.

The other factor that comes into play on how long a storage tank will last is the quality of the fabrication. A properly designed and fabricated FRP tank that is of high quality can be expected to last over 20 years. A poorly fabricated tank may last only 5 -10 years.

ACKNOWLEDGEMENTS

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REFERENCES

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2. ASTM C-581 Standard Practice for Determining Chemical Resistance of Thermoset Resins used in Glass-Fiber Reinforced Structures Intended for Liquid Service, Annual Book of ASTM Standards, July, 2003.
3. Don Kelley, “Fiberglass Reinforced Plastic Equipment for Treating Waste Incineration Gases”, Corrosion 2004 paper # 04617,(Houston, TX, NACE, 2004)

TABLE 1
TEST RESULTS AFTER 12 MONTHS IN 10% SODIUM HYPOCHLORITE AT 50°C

Resin Type	BREVER1	BREVER1	BREVER1	BREVER2
Cure System	CoNap/MEKP	BPO/DMA	BPO/DMA	BPO/DMA
Veil Type	Polyester	Polyester	C-Glass	C-Glass
Flexural Strength Retention, %	66	104	93	83
Flexural Modulus Retention, %	79	101	93	87
Surface Hardness Retention, %	73	100	98	96
Surface appearance	Flat	Flat	Semi-Gloss	Semi-Gloss
Resin Attack	Moderate	Slight	None	None

Resin Type	EVER1	EVER2	NEVER
Cure System	BPO/DMA	BPO/DMA	BPO/DMA
Veil Type	C-Glass	C-Glass	C-Glass
Flexural Strength Retention, %	98	93	88
Flexural Modulus Retention, %	104	93	93
Surface Hardness Retention, %	93	98	76

Surface appearance	Slightly flat	Slightly flat	No gloss
Resin Attack	Slight	Slight	Moderate, only 40% of edge coating remains

TABLE 2
TEST RESULTS AFTER 12 MONTHS IN 10% SODIUM HYPOCHLORITE STORAGE TANKS IN THRONTON, CO

Resin Type	BREVER1	BREVER1	BREVER1	BREVER2
Cure System	CoNap/MEKP	BPO/DMA	BPO/DMA	BPO/DMA
Veil Type	Polyester	Polyester	C-Glass	C-Glass
Flexural Strength Retention, %	90	97	113	98
Flexural Modulus Retention, %	85	100	109	92
Surface Hardness Retention, %	119	114	113	112
Resin Attack	Slight	None	None	None

Resin Type	EVER1	EVER2	NEVER
Cure System	BPO/DMA	BPO/DMA	BPO/DMA
Veil Type	C-Glass	C-Glass	C-Glass
Flexural Strength Retention, %	81	83	103
Flexural Modulus Retention, %	93	92	100
Surface Hardness Retention, %	108	108	106
Resin Attack	Very slight	Very slight	Slight

TABLE 3
TEST RESULTS AFTER 12 MONTHS IN 10% SODIUM HYPOCHLORITE STORAGE TANKS IN CITY OF WESTMINSTER, CO

Resin Type	BREVER1	BREVER1	BREVER1	BREVER2
Cure System	CoNap/MEKP	BPO/DMA	BPO/DMA	BPO/DMA
Veil Type	Polyester	Polyester	C-Glass	C-Glass
Flexural Strength Retention, %	84	88	131	88
Flexural Modulus Retention, %	85	94	103	89
Surface Hardness Retention, %	111	100	113	105
Resin Attack	Slight	None	None	None

Resin Type	EVER1	EVER2	NEVER
Cure System	BPO/DMA	BPO/DMA	BPO/DMA
Veil Type	C-Glass	C-Glass	C-Glass
Flexural Strength Retention, %	107	87	105
Flexural Modulus Retention, %	98	89	99
Surface Hardness Retention, %	110	100	106
Resin Attack	Very slight	Very slight	Slight

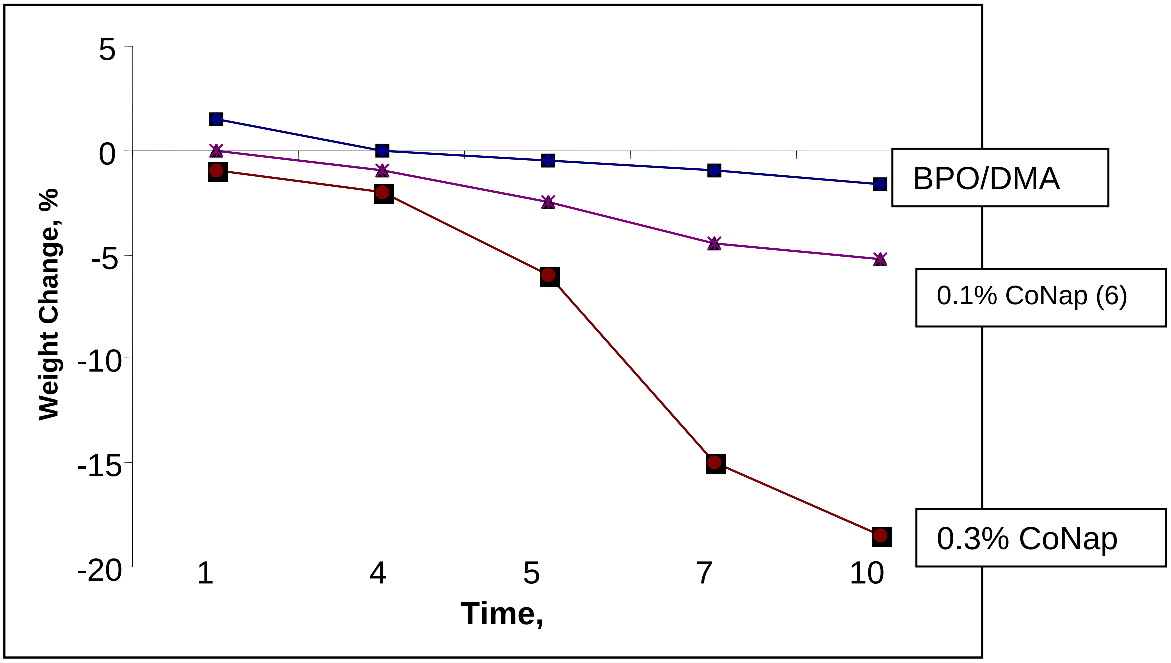

FIGURE 1 – Weight change vs time of bisphenol A epoxy vinyl ester resin coupons exposed to 5.25% sodium hypochlorite at 65°C.

TABLE 4
TEST RESULTS AFTER 12 MONTHS IN 10% SODIUM HYPOCHLORITE AT 65°C

Resin Type	BREVER1	BREVER1
Cure System	BPO/DMA	BPO/DMA
Veil Type	Polyester	C-glass
Flexural Strength Retention, %	29	71
Flexural Modulus Retention, %	26	65
Surface Hardness Retention, %	0	47
Surface Attack	Moderate	Slight